

# Mine Waste Characterization and Drainage Mitigation

## Research Summary 2001

Kim Lapakko  
David Antonson  
Emmelyn Leopold  
Michael Berndt

Minnesota Department of Natural Resources  
Division of Lands and Minerals  
Reclamation Section

*1525 3rd Ave. E.  
Hibbing, MN 55746  
(218) 262-6767*



*500 Lafayette Road  
St. Paul, MN 55155-4045  
(651) 296-4807*

## TABLE OF CONTENTS

LIST OF TABLES	iii
LIST OF FIGURES	iii
0. SUMMARY	iv
1. INTRODUCTION: MINING IN MINNESOTA	1
2. BACKGROUND	4
2.1. Mine waste dissolution chemistry	4
2.1.1. Iron sulfide mineral oxidation.	4
2.1.2. Sulfate mineral dissolution.	4
2.1.3. Neutralization reactions.	5
2.1.4. Trace metal sulfide oxidation.	6
2.2. Mineral dissolution literature summaries	7
2.3. Mine waste characterization.	7
3. DRAINAGE QUALITY FROM MINE WASTES	9
3.1. Taconite tailings drainage quality.	9
3.2. Duluth Complex mine waste drainage.	10
3.2.1. Introduction.	10
3.2.2. Field data.	11
3.2.3. Laboratory predictive tests.	15
3.2.4. Comparison of field and laboratory data on Duluth Complex rock.	19
3.3. Drainage quality from greenstone belt gold mine tailings and waste rock.	20
3.3.1. Tailings	21
3.3.2. Waste rock	22
3.4. Siltite-argillite waste rock.	22
3.5. Mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks.	23



## LIST OF TABLES

1. Summary of solids that have acidified during prolonged kinetic testing. . . . . 29

## LIST OF FIGURES

1. Selected bedrock formations of northern Minnesota . . . . . 2
2. Annual median pH vs. time for the AMAX test piles. . . . . 14
3. Minimum drainage pH decreased as sulfur content increased in the drill  
core solids. . . . . 16
4. Minimum drainage pH decreased as sulfur increased in the blast hole solids. . . . . 17
5. The minimum drainage pH of the blast hole solids in the laboratory were  
consistent with observed values in the field . . . . . 19
6. Map depicting passive and active mitigation at the Dunka Mine . . . . . 33

## 0. SUMMARY

Minnesota presently has a large taconite mining industry, as well as potential for mining of nonferrous minerals, particularly within the Duluth Complex and the greenstone belts in the northern part of the state. Mine wastes that produce problematic drainage must be managed such that the quality of waters of the state is not adversely impacted. Mine waste management strategies directed at this objective include prevention, control, and treatment of problematic drainage. The Reclamation Section within the Division of Lands and Minerals of the Minnesota Department of Natural Resources (MN DNR) has conducted numerous studies on mine waste characterization, drainage quality prediction, and mitigation of mine waste drainage, as well as field studies on the release and aqueous transport of mining related contaminants. These studies were summarized by Lapakko et al. (1998), and the present report extends this summary through 2001.

Although few water quality problems have been associated with the taconite mining industry, there has been recent interest in disposing of tailings in open pits rather than in surface tailings basins, as has been the historical practice. Water would pass from these pits into the Biwabik Iron Formation, which is a major regional aquifer. Consequently, the potential ground water quality impacts of in-pit taconite tailings disposal was investigated in a four year field and laboratory study. Elements of potential environmental and/or health concern were identified and the transport of each of these elements was determined using extensive chemical and isotope data and computer aided modeling techniques.

A process for characterizing potential mine wastes prior to nonferrous mine development was also developed. The characterization process includes performance of dissolution tests to predict the drainage quality from mine wastes. Studies have been conducted to examine the design of such tests and interpretation of their results. Studies have been conducted to determine the quality of drainage from mine wastes from several different rock types. Field studies on the dissolution of Duluth Complex rock have been conducted since the mid-1970's at the Dunka mine and on test piles at the MN DNR Babbitt Research Site until 1994. Laboratory studies have been conducted to describe the quality of drainage by tailings generated from copper-nickel and titanium-oxide deposits of the Duluth Complex, gold deposits from greenstone belts, and by waste rock from Duluth Complex, greenstone and other mining lithologies in the United States.

The use of alkaline solids and subaqueous disposal have been examined for their potential in the environmental management of mine wastes. Laboratory experiments were conducted to examine the mitigative potential of mixing alkaline solids (carbonates) with acid-producing mine waste. Laboratory and field tests were conducted to determine the effectiveness of limestone beds for treating mine waste drainage. Operational scale mitigation measures implemented at the Dunka mine and the AMAX/Kennecott site have been summarized. Finally, disposal of sulfidic rock in a subaqueous setting, with and without various amendments, is under investigation in both the laboratory and field.

New research needs are arising and the complexity of mine waste research has increased substantially since the research program was initiated. These developments required more effort, much of which is at a highly technical level, in order to evaluate, advance, and apply state-of-the-art techniques of environmentally sound mine waste management in Minnesota. The MN DNR (1999), as a result, has developed a long term research plan with the specific goals of meeting this challenge. Communication is maintained with other US and international efforts (Hornberger et al. 2000; Lapakko 2001a) and through cooperative research efforts (MN DNR 2000).

## 1. INTRODUCTION: MINING IN MINNESOTA

Minnesota has an extensive mining industry and potential for mineral expansion and diversification. Iron mining began in Minnesota over a century ago and led to the taconite mining industry which, in 1996, shipped 45 million long tons of iron ore valued at 2.4 billion dollars (Minnesota Department of Revenue 1997). Nonferrous mining development shows promise for the future. The state is presently the subject of extensive metallic mineral exploration, with 267 leases covering over 80,000 acres of state land (Rice 2001).

Considerable mineral potential for base and precious metals is associated with Minnesota's Precambrian rocks, specifically its Archean metavolcanics, metasedimentary formations and the Duluth Complex (figure 1). The Archean metavolcanic and metasedimentary formations, or greenstone belts, of Minnesota extend north into Canada, where they have yielded substantial mineral production. These formations are potential hosts for gold, zinc-copper massive sulfides with various by-products, and magmatic sulfide deposits containing copper, nickel and platinum group elements. Recent exploration of greenstone belt metasedimentary formations has focused on gold, base metals, and silver-cobalt-copper deposits. The Duluth Complex contains an estimated copper-nickel resource of 4.4 billion tons (Minnesota Environmental Quality Board 1979), as well as significant titanium resources. Drill core analyses have also revealed the presence of chromium, vanadium, cobalt, and platinum group elements.

If mineral development occurs, tailings and waste rock, as well as the mine itself will be wastes remaining after the operation is abandoned. Some mining wastes are relatively stable chemically and, therefore, are environmentally innocuous with respect to release of acid and trace metals. On the other end of the spectrum are wastes at mine sites classified by the U.S. Environmental Protection Agency as Superfund Sites. Some of these sites were abandoned in the 1800's and have generated problematic drainage for roughly a century.

Since mine waste drainage quality is variable, the degree of mitigation required for wastes is variable. In order to design and optimize mitigation methods, the quality of drainage from potential mine wastes must be predicted prior to mineral resource development. The optimal method of predicting the quality of drainage from a mine waste is to study drainage from mining wastes of similar composition in the environment over an extended time period. Due to the absence of mining wastes of appropriate composition, as well as time and economic constraints, such an approach is often infeasible prior to mine development. Consequently, it is necessary to predict mine waste drainage quality based on the composition and laboratory dissolution testing of the mine waste. Since, there are no simple tests which can predict the quality of drainage from all mine wastes, expertise is required in design and interpretation of mine waste drainage quality predictive tests.

Mine waste drainage quality, as well as techniques of impact mitigation, have been studied in Minnesota since the mid-1970's. The studies were initiated in 1976 under the auspices of the Regional Copper-Nickel Study and, in 1978, were continued by the Minnesota Department of Natural Resources, Division of Minerals (MN DNR).

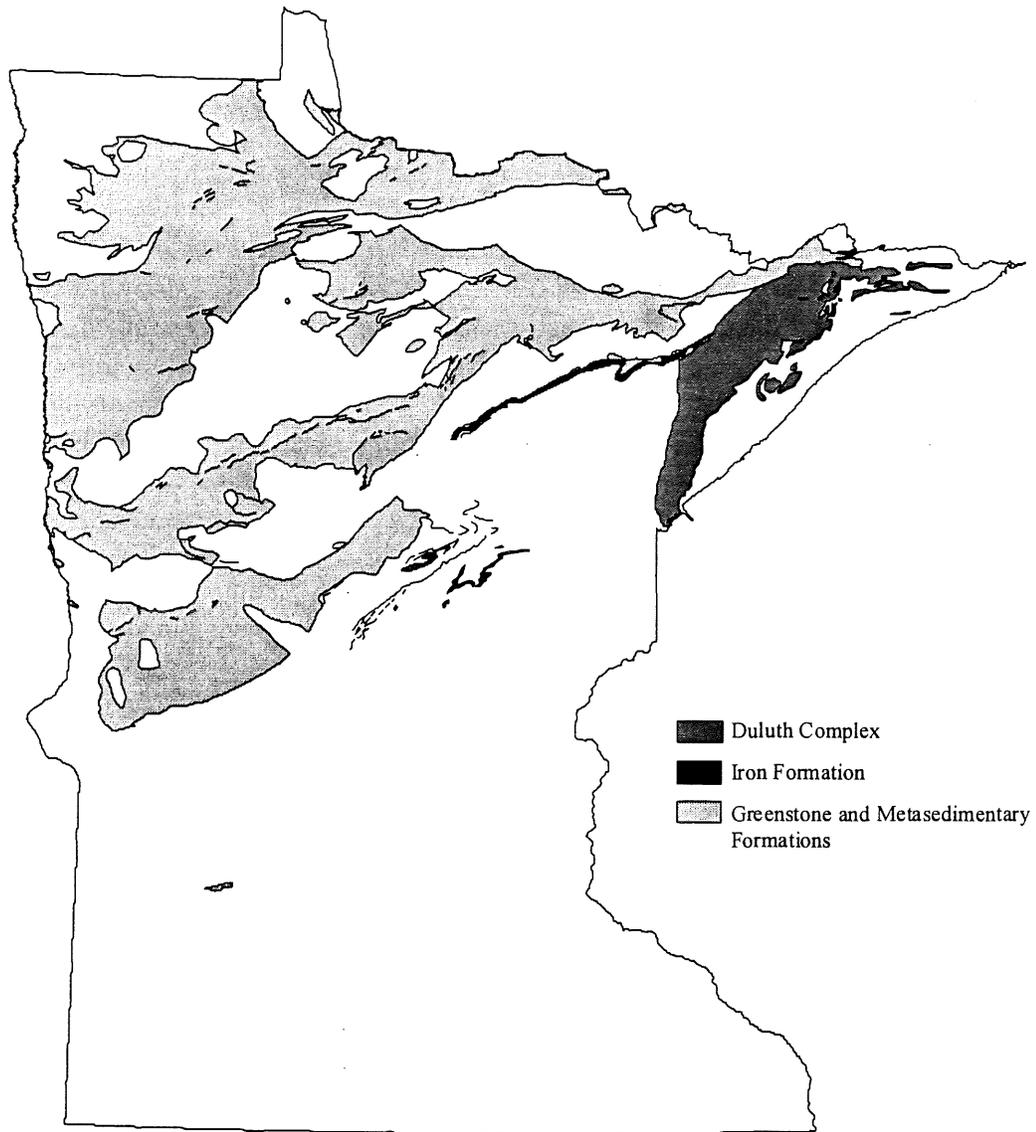


Figure 1. Selected bedrock formations of northern Minnesota (adapted from G.B. Morey et al., 1966).

Many of the studies conducted by the MN DNR were in cooperation with industry or other governmental agencies (Lapakko and Brice 1998). This report summarizes research on:

- mine waste characterization,
- prediction of drainage quality from taconite mining wastes,
- prediction of drainage quality from Duluth Complex mining wastes,
- prediction of drainage quality from greenstone belt mining wastes,
- prediction of drainage quality from other waste rock lithologies,
- evaluation of predictive tests, and
- mitigation of mine waste drainage using alkaline solids and subaqueous disposal.

The results of the studies, many of which are yet in progress, are summarized following a brief discussion of mine waste dissolution chemistry. The information generated in these studies will aid in the prediction and mitigation of acid and trace metal release from mine wastes generated by future operations.

## 2. BACKGROUND

### 2.1. Mine Waste Dissolution Chemistry

#### 2.1.1. Iron sulfide mineral oxidation.

When metal sulfide minerals are exposed to the oxidizing conditions present in waste rock stockpiles, mine walls, and tailings basins, sulfide is oxidized and the associated metals (Fe, Cu, Ni, Co, Zn) are released (Nelson 1978; Garrels and Christ 1965; Sato 1960a, 1960b). Acid is produced as a result of the oxidation of iron sulfide minerals present in mine waste, as indicated by reaction 1 (Nelson 1978) and reaction 2 (Stumm and Morgan 1981). Two moles of acid are produced for each mole of sulfur oxidized.



The rate of iron sulfide oxidation by oxygen is proportional to the available sulfide surface area (Nelson 1978; Sato and Mooney 1960; Sato 1960a, 1960b), and dissolved oxygen concentration (Nelson 1978; Dobrokhotov and Maiorova 1962; McKay and Halpern 1958), with only a slight dependence on pH (Nelson 1978; Majima and Peters 1966). These oxidation reactions can elevate aqueous concentrations of iron, sulfate, and acid. These components can 1) accelerate the oxidation of other sulfide minerals, 2) precipitate hydrated iron-sulfates or other minerals, 3) contact host rock minerals which react to neutralize some or all of the acid, and/or 4) exit the mine waste as acidic flow, referred to as acid mine drainage (AMD) or acid rock drainage (ARD).

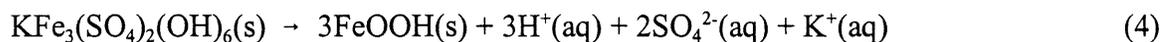
Ferric iron oxidizes iron sulfides more rapidly than oxygen (Singer and Stumm 1970). Research on pyrite oxidation indicates that as "pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent" (Nordstrom 1982). As pH further decreases, bacterial oxidation of ferrous iron becomes the rate-limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm 1970), which is the only significant oxidizing agent in this pH range (Nordstrom 1982; Singer and Stumm 1970; Kleinmann et al. 1981). Under these conditions the reaction is independent of sulfide-mineral surface area (Singer and Stumm 1970).

#### 2.1.2. Sulfate mineral dissolution.

Hydrated iron sulfate minerals may precipitate due to evaporation of acidic, iron- and sulfate- rich water within mine wastes. This essentially stores acid generated by iron sulfide mineral oxidation for potential subsequent release. The more common of these minerals that occur as efflorescent salts on the surfaces of weathering pyrite include melanterite, rozenite, szomolnokite, romerite, and copiapite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$ , and

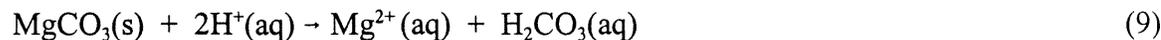
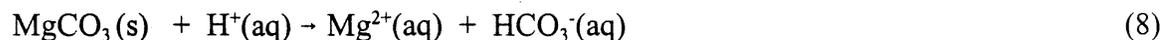
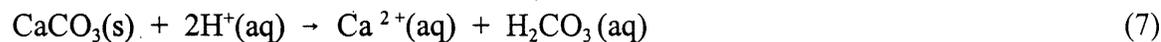
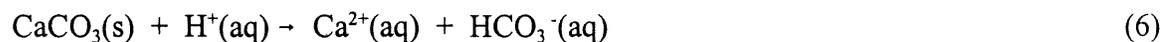
$\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$  respectively; Alpers et al. 1994). These salts are highly soluble and provide an instantaneous source of acidity upon dissolution (Nordstrom 1982, Cravotta 1994). For example, dissolution of one mole of melanterite contributes two moles of acid (reaction 3). Similarly, Cravotta (1994) reported that dissolution of one mole of romerite produces six moles of acid. Reactions such as this may be largely responsible for increased acidity loadings during rainstorm events.

The formation of hydrated iron sulfates is an important intermediate step that precedes the precipitation of slightly soluble iron minerals such as jarosite (Nordstrom 1982). Jarosite is slightly soluble (Alpers et al. 1994) and yields 1.5 moles of  $\text{H}^+$  per mole dissolved (reaction 4). In studies conducted at the U.S. Bureau of Mines, Salt Lake City Research Center (USBM SLRC), the pH of deionized water dropped from 6 to 3 or 4 after contact with synthetic and natural jarosites (White et al. 1997a). Because of jarosite's relatively low solubility, the acid contributed by its dissolution is probably small relative to that by dissolution of more soluble hydrated iron sulfates. It should be noted that sulfate minerals such as anhydrite ( $\text{CaSO}_4$ , reaction 5) or barite ( $\text{BaSO}_4$ ) will not produce acid.



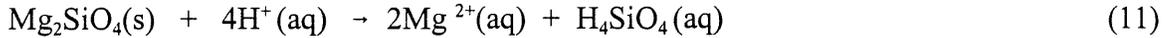
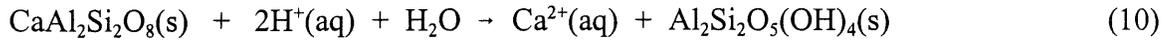
### 2.1.3. Neutralization reactions.

The most effective minerals for neutralizing acid are calcium carbonate and magnesium carbonate (reactions 6-9). Reactions 6 and 8 are dominant above approximately pH 6.3, while reactions 7 and 9 are dominant below this pH.

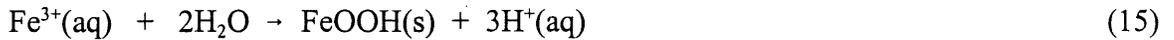
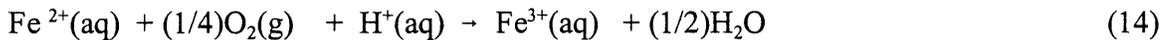
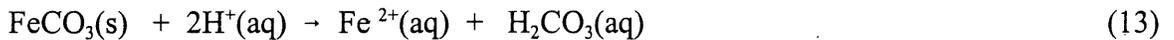
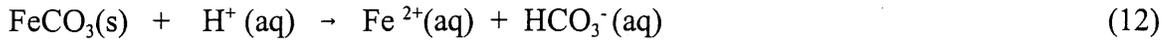


Other minerals, such as anorthite and forsterite, can also consume acid but their dissolution rate (and associated rate of acid neutralization) is typically slow in the neutral pH range (reactions 10, Holdren

and Berner 1979; and reaction 11, Hem 1970). These minerals dissolve more rapidly as pH decreases, and therefore, provide more buffering under acidic conditions.

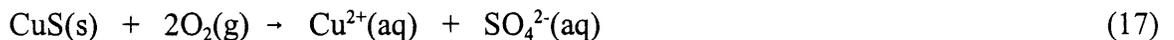


Iron carbonates will provide no net neutralization of acid. The initial dissolution of one mole of iron carbonate will consume one or two moles of acid (reactions 12, 13). However, under environmental conditions the one mole of ferrous iron released will oxidize to ferric iron (reaction 14) which will precipitate as ferric oxyhydroxide (reaction 15). The oxidation of ferrous iron is slower than the subsequent ferric oxyhydroxide precipitation, and is reported to be second-order with respect to hydroxide ion concentration (Sung and Morgan 1980; Eary and Schramke 1990). The oxidation and precipitation reactions will yield two moles of acid (reaction 16). Thus, iron carbonate will not contribute to acid neutralization.



#### 2.1.4. Trace metal sulfide oxidation.

The oxidation of trace metal sulfide minerals releases trace metals and sulfate but does not necessarily contribute acid (reaction 17). Reactions subsequent to sulfide mineral oxidation affect



the net trace metal release to the environment. The transport of a given component in the environment is the net result of release to solution by dissolution and removal from solution by precipitation, coprecipitation, exchange reactions, and adsorption. The degree of trace metal transport is dependent upon drainage composition (particularly pH), the chemistry of the released component, and the chemical character and surface area of solid surfaces present. Concentrations of trace metals tend to increase exponentially as solution pH decreases, therefore acidic drainages often contain elevated trace metal concentrations. However, circumneutral drainages can contain elevated concentrations of trace metals such as nickel (Eger and Lapakko 1985) and molybdenum (Brown 1989) which, compared to other trace metals, are relatively soluble in this pH range.

Chemical release is also affected by the amount of water percolating through the stockpile, which is dependent on the input volume and subsequent flow routing. Precipitation is an ever present input, but surface water and groundwater can also contribute under certain conditions. The water input will be incorporated as storage or discharged as evapotranspiration, surface runoff, subsurface flow (interflow) or baseflow (Hewett 1980).

## **2.2. Mineral dissolution literature summaries.**

Extensive research has been conducted elsewhere that may benefit environmental mine waste management in Minnesota. Thus, a series of annotated bibliographies was generated to identify and help summarize those studies most relevant to reactions taking place or expected to be taking place in Minnesota tailings and waste rocks. These include acid-producing reactions involving oxidative dissolution of pyrite (Jakel and Lapakko 1999a; Leopold and Lapakko 2001a) and pyrrhotite (Jakel and Lapakko 1999b; Leopold and Lapakko 2001b) and acid-neutralizing reactions involving carbonates (Doctor et al. 2001) and silicates (Phillips et al. 2001).

## **2.3. Mine waste characterization.**

The quality of mine waste drainage is variable, largely due to the variability in mine waste composition. By characterizing mine wastes and predicting mine waste drainage quality prior to mineral resource development, waste disposal facilities can be designed, sited, constructed, and reclaimed in a manner that will most effectively reduce contaminant release and the associated drainage treatment cost. Mitigation can be tailored to the predicted drainage quality and directed toward meeting water quality objectives. Wastes with mitigative capacity (e.g. limestone) can be identified during the characterization process. Finally, the cost of reclamation can be considered along with other mining costs in the assessment of resource development economics. Mine development can then progress with consideration of both metal recovery and the environmentally sound management of mine wastes.

A mine waste characterization process was designed for application on a site specific basis (Lapakko 1990b, 1988b). The approach and analytical techniques used are similar to those employed for evaluation of potential for resource recovery. The extent of rock units potentially contributing to mine waste is delineated and pertinent compositional aspects of these units are quantified. The quality of drainage from the potential wastes is then projected. Existing data on a mine waste of similar composition, generated by similar mining methods, and exposed to similar environmental conditions for an extended time provide the best indicator of drainage quality. A directory of contacts was compiled to facilitate collection of information on mine waste composition and drainage quality across the United States (Wessels et al. 1991).

Since data on the drainage quality from a mine waste of specific composition are often not available, it is commonly necessary to conduct laboratory dissolution tests to predict drainage quality. These tests could be conducted on a variety of representative samples from individual rock units to

determine the relationship between mine waste composition and drainage quality. Additional sampling, analysis, and dissolution testing may be required based on the information compiled. The relationship between solid composition and chemical behavior is then extrapolated to the waste as a whole. A mine waste management program would be designed based on the projected drainage quality and quantity.

The mine waste composition and predicted drainage quality would be subject to verification during operation if mine development proceeded. Small scale field tests on well-characterized waste allow more accurate extrapolation to operational scale drainage quality and drainage volume, and also allows assessment of mitigation design. Initiating such tests as soon as resource development begins, maximizes the benefit of these tests for drainage quality prediction and mine waste management.

### **3. DRAINAGE QUALITY FROM MINE WASTES.**

As mentioned previously, Minnesota has an extensive taconite mining industry. The mines, tailings, and waste rock produced during this mining cover more than 135 square miles. Despite the vast amount of these wastes, drainage quality problems have been minimal. Studies have been conducted to quantify the sulfate released with drainage from a tailings basin and to evaluate ground water quality impacts of disposing taconite tailings in existing open pits.

Potential for base and precious metal development is associated with the Duluth Complex and the greenstone belts (greenstones and metasedimentary formations) of Minnesota (figure 1). The Duluth Complex holds potential for development of copper-nickel, titanium, platinum group elements (PGE) and dimension stone resources, and the greenstone belts are potential sources of base and precious metals. Field drainage quality data have been collected from Duluth Complex waste rock in operational stockpiles, small scale test piles, and dimension stone quarries. Extensive laboratory testing has been conducted to better understand dissolution of Duluth Complex rock and titanium tailings, as well as gold mine tailings from greenstone belts. Dissolution testing of rock types outside of Minnesota has also been conducted with funding from the US Bureau of Land Management.

#### **3.1. Taconite tailings drainage quality.**

Drainage quality from taconite mining wastes generally meets water quality standards. In part, this reflects the chemically stable nature of these wastes when exposed to conditions at the earth's surface. Upon examination of existing data, Lapakko and Wagner (1989) reported that trace metal concentrations in drainage from Minnesota iron mining wastes are generally low. This observation was attributed to the low trace metal concentrations in the iron formation and the neutral pH of drainage from the taconite waste rock and tailings. Two studies have been conducted on the quality of drainage from taconite tailings. The first study quantified sulfate release in seepage from a taconite tailings basin, identified sulfate sources, and estimated contributions from the various sources (Lapakko and Jagunich 1991).

The second study addressed the potential ground water quality impacts of disposing taconite tailings into open pits (Berndt and Lapakko 1997a, 1997b; Jakel et al. 1998a, 1998b; Berndt et al. 1998a, 1998b, 1999; Jakel and Lapakko 1999c). It was thought that in-pit disposal might involve release of metals or organic compounds into the Biwabik Iron Formation regional aquifer due to enhanced tailings dissolution and/or input of organic reagents used in taconite processing. In the first phase of the study existing water quality data from taconite operations were examined; additional operational samples were collected and analyzed for 82 inorganic parameters and up to 180 organic parameters; laboratory and field experiments were conducted; and geochemical equilibrium models were developed using the water quality compositions observed. Fluoride, arsenic, molybdenum and manganese were identified as potentially problematic inorganic parameters within the pit boundary. No potentially problematic organic parameters were identified.

In the second phase of the study, monitoring and experiments were continued for a longer term and new experiments were conducted to evaluate chemical processes deemed important in the first phase of the study. Manganese oxidation kinetics were examined for high-Mn water in contact with the atmosphere (Jakel and Lapakko 1999d). Bench-top flow through experiments were conducted to help quantify fluoride adsorption to tailings (Berndt et al. 1999). Carbon isotope measurements were made and then used to quantify the relative sources of organic and inorganic carbon in tailings basins and seeps, as well as in experiments (Berndt et al. 1999). These isotope measurements revealed that high Mn in waters seeping from one of the tailings basin was most likely related to decay of buried plant matter rather than to reaction with the tailings themselves. Experiments were also conducted to evaluate the potential effects of rainwater and groundwater that might penetrate into tailings after in-pit disposal facilities are closed (Berndt et al. 1999; Leopold and Lapakko 2001c). Fluid chemistry and hydrogen and oxygen isotopes were also measured for wells in the Biwabik Iron Formation to identify key reactions taking place within this aquifer and also to provide much needed background data on a wide variety of elements (Berndt et al. 1999).

Finally, an analogue for in-pit deposition of taconite tailings was located on the US Steel (USX) mining property near Mountain Iron Minnesota. A well was drilled deep into the tailings in 1996 and surface and pore waters associated with this site were collected and analyzed for the next two years until the entire pit and contents were removed by more recent mining efforts. Detailed chemistry of the Snively Pit history, including hydrology and chemistry over the last several years of its life were presented by Berndt and Lapakko (1997 a,b) and Jakel and Lapakko (1999e). As is apparent from the previous paragraphs, a large amount of data was generated over the course of the study. To digest results generated over the first three years of the project, information on predicted water quality in open pits into which taconite tailings are disposed was summarized in 1998 (Lapakko et al. 1998).

Disposal of taconite tailings into the Minorca Pit was proposed by Inland Steel. This activity would possibly affect water quality in the nearby Missabe Mountain Pit which serves as the water supply for Virginia, Minnesota. Based largely on results from the above studies, potential effects on water quality in the Missabe Mountain Pit were summarized (Lapakko and Jakel 1999) and analyzed in detail (Lapakko and Jakel 2000). These reports concluded that none of the identified parameters of concern (fluoride, arsenic, molybdenum, manganese) would exceed standards.

## **3.2. Duluth Complex mine waste drainage.**

### **3.2.1. Introduction.**

The Duluth Complex is a massive gabbroic intrusion in northeastern Minnesota containing low grade copper and nickel sulfides, titanium oxides, and platinum group elements. It has also been developed as a source of dimension stone. The Complex contains one of the largest known copper and nickel resources in the U.S. (Minnesota Environmental Quality Board 1979; Kingston et al.

1970). In 1976, The Regional Copper-Nickel Study was formed in response to public concerns regarding the environmental impact of copper-nickel mining. The final summary report was completed in 1979 (Minnesota Environmental Quality Board 1979). The investigations conducted included operational scale field studies at the Dunka Mine (an active iron ore operation), pilot scale field studies at the AMAX exploration site, monitoring of a bulk sample site, as well as laboratory experiments.

The earliest reports on the Duluth Complex focused on the impact of potential copper-nickel mining (Thingvold et al. 1979), and addressed the hydrology (Hewett 1980) and chemistry of stockpiles. The early laboratory studies (Lapakko 1980; Eisenreich et al. 1977a, 1977b) investigated the kinetics and mechanisms of gabbro dissolution as well as trace metal equilibria. The findings of the early field monitoring, the laboratory experiments, and the chemical equilibrium computer models were compiled in a comprehensive report (Eger and Lapakko 1980c), and summarized in shorter papers presenting the chemical mechanisms of leaching (Lapakko and Eger 1980a, 1980b).

The following presentation indicates that Duluth Complex rock with sulfur contents greater than or equal to 0.41 wt % produced drainage pH values below 6.0 in laboratory tests. Samples with sulfur contents of 0.18, 0.22 and 0.40 percent produced drainage pH values above 6.0. Consideration of laboratory and field test pile data suggest a threshold sulfur content of 0.2 to 0.4 percent in the field. Sulfur contents exceeding this critical value would produce acidic drainage, while those below it would not. It was not possible to verify this relationship for field-scale wastes at the Dunka site, due to uncertainty in the waste rock sulfur contents. Trace metal release in neutral drainage must also be considered in addressing the impacts of Duluth Complex drainage on water quality.

### 3.2.2. Field data.

Field water quality data were collected at an operational taconite mine where Duluth Complex rock had been stripped and stockpiled, at six test piles, and at dimension stone quarries. **Operational scale Duluth Complex rock stockpiles** are present at LTV Steel Mining Company's (previously Erie Mining Company) Dunka Mine, a full-scale open pit taconite operation near Babbitt, Minnesota. The Dunka open pit intersects the geological contact between the Duluth Complex and the Biwabik Iron Formation, and removal of Duluth Complex rock was required to mine the underlying taconite. More than 50 million tons of the sulfide-mineral-bearing rock is stored at the site, in stockpiles which cover 320 acres.

Since 1976, data have been collected on the drainage quality, quantity, and chemical mass release associated with stockpile drainages at the site. The initial data were collected by the Regional Copper-Nickel Study (Thingvold et al. 1979), and after 1980 the monitoring was conducted by Erie Mining Company and LTV Steel Mining Company. The most recent report (MN DNR 1996, unpublished) presented the results of monitoring from 1976 to 1993, and earlier reports are available (MN DNR 1987, 1994; Eger et al. 1981b; Eger and Lapakko 1980a; Eger et al. 1977). Other studies at the Dunka site have focused on the transport of trace metals leached from the stockpiles through

a white cedar swamp (Eger et al. 1980a; Eger and Lapakko 1988, 1989), Unnamed Creek (Eger and Lapakko 1980b; Strudell 1986), and Bob Bay (Lapakko and Eger 1981b; Strudell et al. 1984; MN DNR unpublished data 1990). Information on the kinetics, mechanisms, and capacities of metal sequestration by peat has been compiled in the form of literature reviews (Lapakko et al. 1986b; Otterson 1978) and laboratory experiments on metal removal by peat have been conducted (Lapakko et al. 1986a).

The most recent report indicates total flow from the watershed is about one billion gallons per year, of which drainage associated with stockpiles has contributed roughly 5 to 20 percent (MN DNR 1996, table 5). During the period from 1976 through 1993, the majority of leachate samples had pH values between 6.0 and 8.5, but values as low as 4.2 were reported (MN DNR unpublished data). Concentrations of trace metals (Cu, Ni, Co, Zn) exceeded ambient levels by 10 to 10,000 times. Nickel contributed more than 90 percent of the trace metal load from the stockpiles, and its subsequent removal by natural processes in the Unnamed Creek system was less than 40 percent. Consequently, in the absence of mitigative measures, nickel concentrations will be elevated downstream from Duluth Complex stockpiles. Concentrations of calcium, magnesium and sulfate in the stockpile drainage were also elevated, but these three parameters are of lesser environmental impact than the trace metals. Indeed, elevated concentrations of calcium and magnesium can reduce the toxic effects of trace metals. Chemical mass release of trace metals from the stockpiles reached a maximum in 1988, when nickel concentrations reached levels as high as 80 mg/L. By 1993, nickel concentrations had decreased to concentrations in the range of 10 to 20 mg/L. This was probably a result of more recent mitigation measures (see Mitigation, Section 5).

**Six small test piles** containing 820 to 1300 metric tons of low grade copper-nickel Duluth Complex rock, taken from an exploration shaft, were constructed next to the MINNAMAX test shaft near Babbitt, Minnesota. Sulfur contents of the test piles were 0.63 (four piles), 0.79 and 1.41 percent. For runoff collection, each pile was underlain by an impervious Hypalon liner. Both drainage flow and quality were determined. In 1982, approximately 40 percent of test pile FL4 was removed for use in another study of stockpile reclamation techniques. In 1994, the piles were dismantled and the rock was incorporated into two concrete/rock monoliths as a final reclamation measure for site closure. During dismantling of three of the piles (FL1, FL5, FL6), rock samples were collected for physical, chemical and mineralogical characterization.

The most recent report on this project (Lapakko 1993b) was published in 1993, although additional progress reports (Eger and Lapakko 1985; Eger et al. 1981a, 1980b, 1979) and symposium publications (Eger and Lapakko 1981; Eger et al. 1980a) are available. The following conclusions on Duluth Complex rock drainage quality from 1978 through 1993 were drawn based on this small scale field monitoring program.

1. Trace metal concentrations in drainage from test piles containing low grade sulfide mineralization exceeded concentrations in undisturbed streams of the area by as much as five orders of magnitude.

2. Drainage pH decreased while trace metal concentrations and mass release rates increased with time and the iron sulfide content of the stockpile (figure 2).
3. For the 16-year period of record, a critical iron sulfide content appears to occur at somewhat less than 1.1 weight percent FeS (0.6 % total S) in the bulk rock. Rock of similar mineralogy and particle size distribution which contained more than this critical amount would generate acidic leachate.
4. The early drainage quality was not an accurate indicator of longer-term drainage quality. For the test piles that contained 0.63% S (FL1, FL2, and FL3), acid producing conditions did not occur for 5 to 6 years. Even after the 16 years of this study, less than 12% of the total sulfur was released from the piles as sulfate. Predictions based on data from the first years of this study would have underestimated trace metal release rates and acid production.

In 1994, the piles were dismantled, and bulk and spatially distributed samples were collected from FL1, FL5, and FL6 (Lapakko et al. 1994). Samples were analyzed for particle size distribution, chemistry (including acid content), and semi-quantitative mineralogy. The objectives of this characterization were to 1) identify physical, chemical, mineralogic, and hydrologic controls on the transport of acid and trace metals from the piles and 2) explain the differences observed between field and lab data. Visual inspection of the piles found elemental sulfur, elemental copper, and a blue green precipitate (possibly a trace metal solid phase), in addition to the expected iron oxyhydroxides and gypsum. Substantial cementation was also observed in the higher sulfur piles, with agglomerates varying in size (1cm to 1m) and cohesiveness. A final report of these results is pending.

Geochemical modeling was used to predict the mineralogic and hydrologic controls on test pile FL1. Nine samples from test pile FL1 were subjected to a sequential extraction procedure that indicated that trace metals released during the oxidation of sulfides were strongly adsorbed to amorphous ferric oxyhydroxides (Kelsey et al. 1996). Predictions, using the geochemical modeling program MINTEQAQ, generally agreed with the sequential extraction results, but did underestimate the extent of nickel adsorption to amorphous ferric oxyhydroxides (Kelsey et al. 1996).

In late 1991, rock and water quality samples were taken from five abandoned and potential **dimension stone quarry sites** in the Ely-Isabella area of northeastern Minnesota. The abandoned sites and two of the potential quarry sites are located in Duluth Complex rock. The third potential site is in the Vermilion Granitic Complex. Total sulfur content of the rocks was less than 0.05 % and trace metal levels were low. Consequently, the pH of water in the abandoned pits ranged from 6.5 to 6.8, and sulfate concentrations were low. Only copper and zinc levels were higher than background levels in the area (Lapakko and Oberhelman 1993). However, all of these parameters were well within water quality standards.

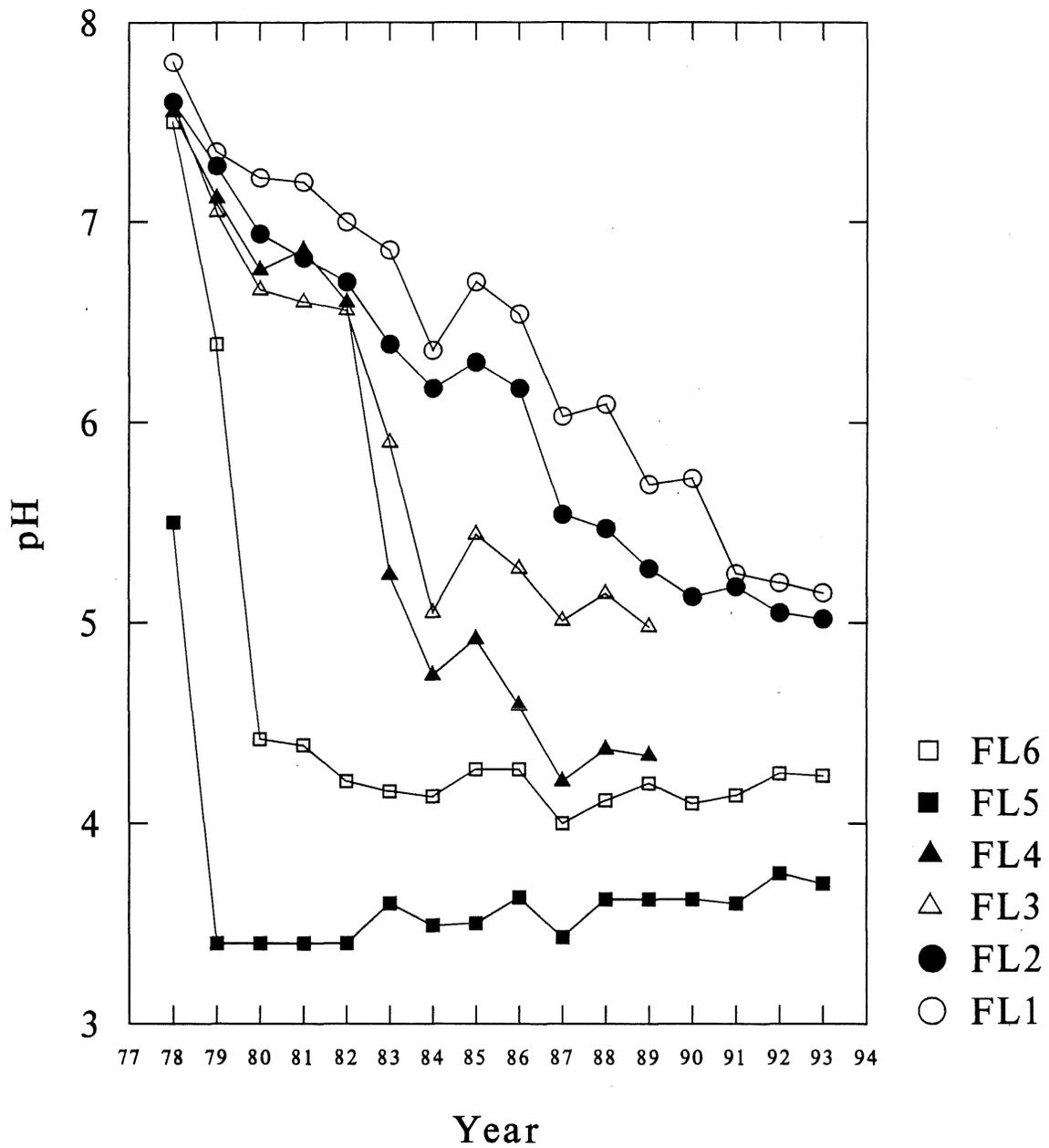


Figure 2. Annual median pH vs. time for the AMAX test piles.

### 3.2.3. Laboratory predictive tests.

The variation of laboratory drainage quality with Duluth Complex rock composition was initially examined in batch reactor and column tests (Lapakko 1980). Subsequently, an experimental method based on the principle that sulfide minerals oxidize in the presence of atmospheric oxygen and water was used (Gottschalk and Buehler 1912; Caruccio et al. 1980). Samples were quite fine, ranging from 0.053 to 0.149 mm in diameter (-100/+270 mesh). Experiments were conducted on 75-g samples in units designed to permit the rinsing of solids and filtration of the rinse solution in one step (U.S. Patent No. 4,783,318). The solids (and reactors) were stored in a controlled temperature and humidity environment, and rinsed weekly with 200-mL volumes of distilled deionized water.

The wet-dry cycle dissolution technique described above was used to investigate the effect of solid phase sulfur content on the quality of drainage from **AMAX drill core samples** of Duluth Complex rock over periods of 30 to 49 weeks (Lapakko 1993e, 1988a). The use of sulfur content alone as the controlling variable for drainage pH assumes that acid neutralization by host rock mineral dissolution is relatively constant in Duluth Complex rocks of similar particle size. The solids examined were divided into three groups based on sulfur content, which ranged from 0.47 to 2.57 percent, maximum rate of sulfate release, and minimum pH of the drainages (Lapakko 1993e).

Group 1 samples contained 0.47 to 0.80% sulfur and produced maximum sulfate release rates of 5.8 to 16  $\mu\text{mol}/\text{week}$ . The sum of calcium and magnesium release rates exceeded the sulfate release rates (that is, the rates of acid neutralization exceeded the rates of acid production) and, consequently, the drainage pH of Group 1 solids remained higher than 6.0 (figure 3). Group 2 (0.92 - 1.26% S) and Group 3 (1.35 - 2.57% S) solids had higher sulfur contents, exhibited higher sulfate release rates (20 to 190  $\mu\text{mol}/\text{week}$ ), and produced minimum drainage pH values in the range of 3.77 to 4.50 (figure 3; note that the 1.26% S solid was weathered rock from a test pile, as opposed to drill core). For all solids examined, less than nine percent of the sulfur in the samples was oxidized (Lapakko 1993e), suggesting that extrapolating the data for long-term predictions was tenuous. The laboratory pH was somewhat higher than expected based on data from the test piles discussed previously.

The composition of the Duluth Complex rock examined in the aforementioned experiment was subsequently characterized using more sophisticated methods (Pignolet-Brandom and Lapakko 1990). The QEM\*SEM automated scanning electron microscope image analysis system was used to quantify the volumetric abundances of iron sulfides, copper-iron sulfides, nickel-iron sulfides, and calcite, as well as the general categories of silicate, oxide and phosphate minerals. The sulfur, nickel, and copper contents based on volumetric abundances were typically within 20 percent of the values determined by standard chemical analyses, indicating that the QEM\*SEM analyses were reasonable. QEM\*SEM can quantify other parameters affecting mine waste dissolution, including mineral grain and rock particle size, particle surface mineralogy, extent of sulfide liberation, as well as total and liberated mineral surface area per unit volume.

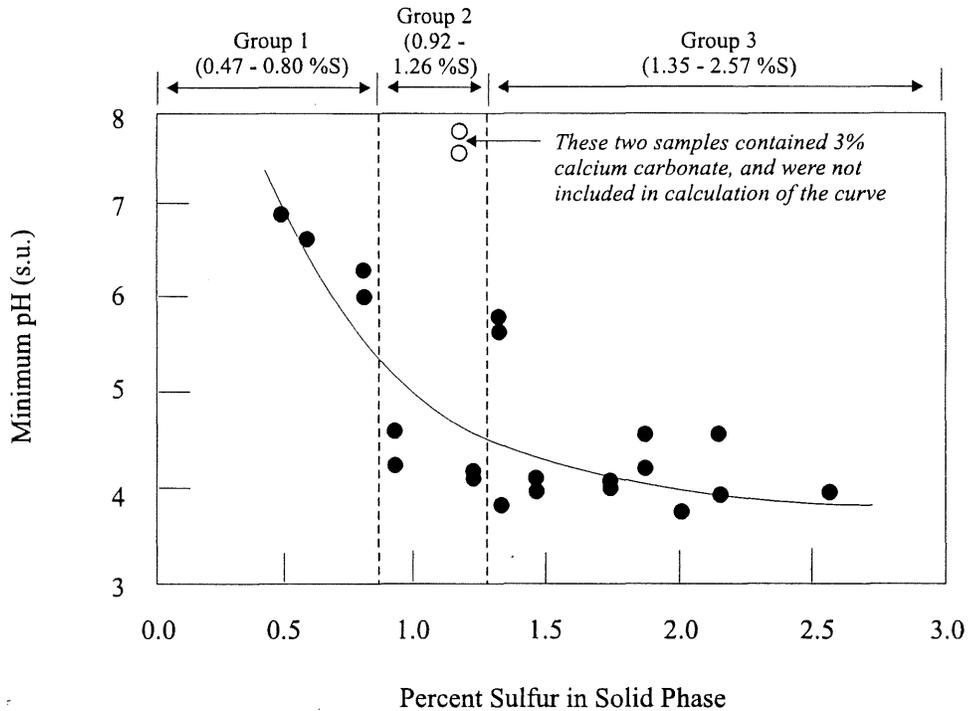


Figure 3. Minimum drainage pH decreased as sulfur content increased in the drill core solids.

The wet-dry cycle dissolution procedure was also used to examine the longer-term drainage quality from sixteen Duluth Complex samples ( $0.18 \leq \text{pct S} \leq 3.12$ ) collected from **blast holes at the Dunka site**. The data for this experiment have been summarized for the first 69, 78, or 150 weeks (periods of record varied for different solids; Lapakko and Antonson 1993; Lapakko 1993a). The rate of sulfate release was approximately first order with respect to the solid phase sulfur content. Minimum drainage pH decreased with increasing solid phase sulfur content and time of reaction (figure 4). Based on drainage pH and sulfate release rates, the rocks were divided into four groups of variable sulfur content. For a 150-week period of record the pH of drainage from Group 1 (0.18-0.40 %S) was continuously above 6.0, while the minimum drainage pH for Group 2 samples (0.41-0.71 %S) ranged from 4.82 to 5.30. The Group 3 samples (1.12-1.64 %S) generated minimum drainage pH values of 4.32 to 4.92 over a period of 69 weeks, while the two Group 4 samples (2.06 and 3.12 %S) generated minimum drainage pH values of 3.5 to 4.3 over a period of 78 weeks (Lapakko and Antonson 1993; Lapakko 1993a).

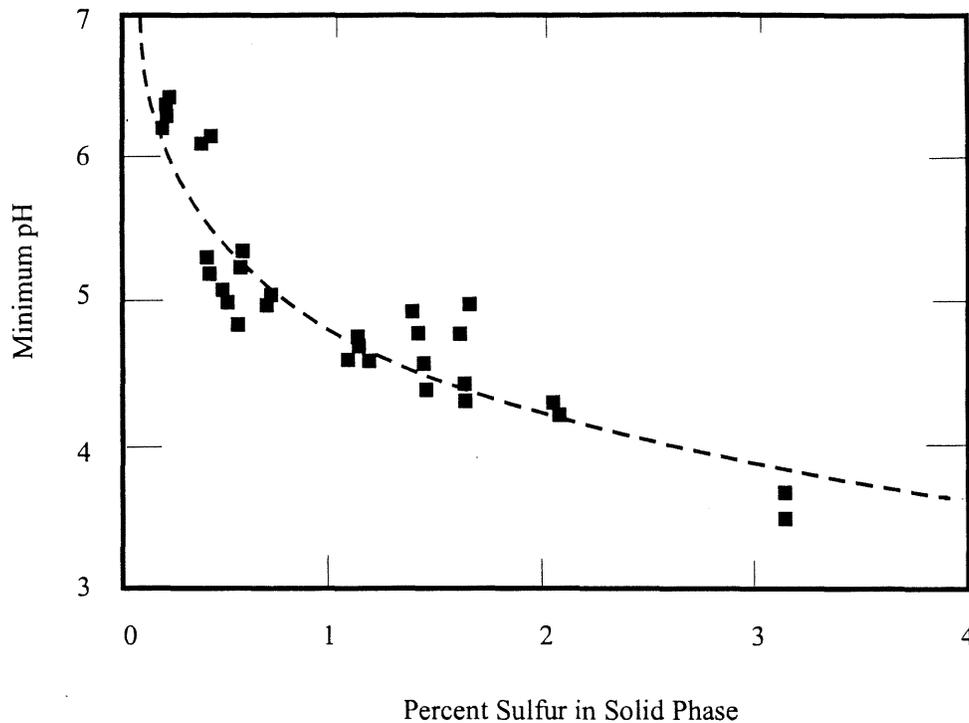


Figure 4. Minimum drainage pH decreased as sulfur increased in the blast hole solids.

Testing of these samples continues (present records of 550 and 650 weeks) to further examine long-term dissolution behavior of the rock (MN DNR Hibbing Laboratory, unpublished data). As of week 630, the samples from the Group 1 have maintained drainage pH values near 6.0. The drainage pH values for the samples in the Groups 2 and 3 continued to drop for roughly 300 to 350 weeks, reaching minimum ranges of 4.0-4.3 and 3.0-3.5, respectively. Drainage pH values from the Group 2 and 3 samples subsequently increased to the typical range of 5.0 to 5.3. Based on minimum pH values the 0.71 percent sulfur sample was moved from its original Group 2 classification to Group 3. The two Group 4 samples were discontinued after 78 weeks. It was noted that solids with similar sulfur-contents produced drainage with similar pH values over the same time period, lending credence to the prediction of drainage pH based on sulfur content of Duluth Complex rock alone (figure 4).

To extend this data base, dissolution testing was initiated in August 1997 on Duluth Complex rock from a bulk sample site and samples of AMAX drill core. Sulfur contents of these samples ranged from 0.67 to 1.71 percent. The 1.71 percent sulfur sample was terminated after 143 weeks and the remaining samples have a 186-week period of record.

Dissolution testing of **larger Duluth Complex particles** ( $d < 0.25$  in.), using a different method (ASTM 5744-96 method), began in July 1992 at the US Bureau of Mines Salt Lake City Research Center (USBM). Tests were conducted on eight Duluth Complex samples which were collected

randomly from the surface of AMAX test piles FL1 and FL6 in 1992. Samples with sulfur contents ranging from 0.56 to 1.39 percent (White 1998), virtually all of which was present as sulfide, were run in duplicate and the duplicates were terminated after 60 weeks. The remaining eight samples were continued for 168 weeks.

Minimum pH values ranged from approximately 4 to 5, and were in general agreement with values observed at MN DNR for samples of similar sulfur content. However, the USBM drainage pH values did not decrease strictly with increasing sulfide content, and the lowest pH values were produced by a sample containing 0.97 percent sulfide. The rates of sulfate, calcium, and magnesium release from the USBM samples were typically 25 to 75 percent of those observed in MN DNR experiments on Dunka blast hole samples of similar sulfur contents. The difference in rates was most likely due to the particle size in the USBM experiments, which was large relative to the 0.053-0.149 mm diameter particles used in the MN DNR experiments. A similar effect of particle size on release rates was observed in an experiment conducted as part of an EPA project (Lapakko et al. 1995). However, in the EPA project drainage pH was also observed to decrease with particle size. In contrast, the drainage pH values from the USBM study were roughly equal to or, in the case of the 0.97 percent sulfide sample, lower than the associated MN DNR samples.

The 1.39-percent sulfur sample underwent further testing at the MN DNR, using method ASTM 5744-96 and three modifications of this method (Lapakko 1998b; Lapakko 1999c; Lapakko and White 2000; White and Lapakko 2000; Lapakko and Antonson 2000a). These experiments, involving different labs and/or using slightly different experimental procedures, yielded similar results for leaching tests performed on the same rock. This reveals that the large differences in the chemistry of leachate fluids are probably related to differences in fluid/rock interaction processes and not to differences in experimental procedures.

Two tailings samples generated from bench scale tests on **titanium ore from the Duluth Complex** were also subjected to solid phase characterization and dissolution testing described above (Lapakko 1991a, 1993c). The test was very preliminary, and since the two tailings were generated from the same ore, the results do not represent the potential range of ore and tailings composition. The tailings were relatively coarse and contained very few sulfide or carbonate minerals. However, they did contain elevated concentrations of chromium, copper, and nickel. The neutralization potentials determined by static tests greatly overestimated the total calcium carbonate and magnesium carbonate content of these two samples.

These tailings generated drainage of neutral pH during the 52-week dissolution test, and presented virtually no potential for acid production since the sulfide content of both samples was reported as less than 0.01 percent. Copper, nickel, and zinc concentrations (to a lesser extent) were elevated in these tailings and in the initial drainage. Concentrations subsequently decreased, suggesting that only a small fraction of the metals present in the solid phase were readily leachable under the conditions of this experiment (Lapakko 1991a, 1993c).

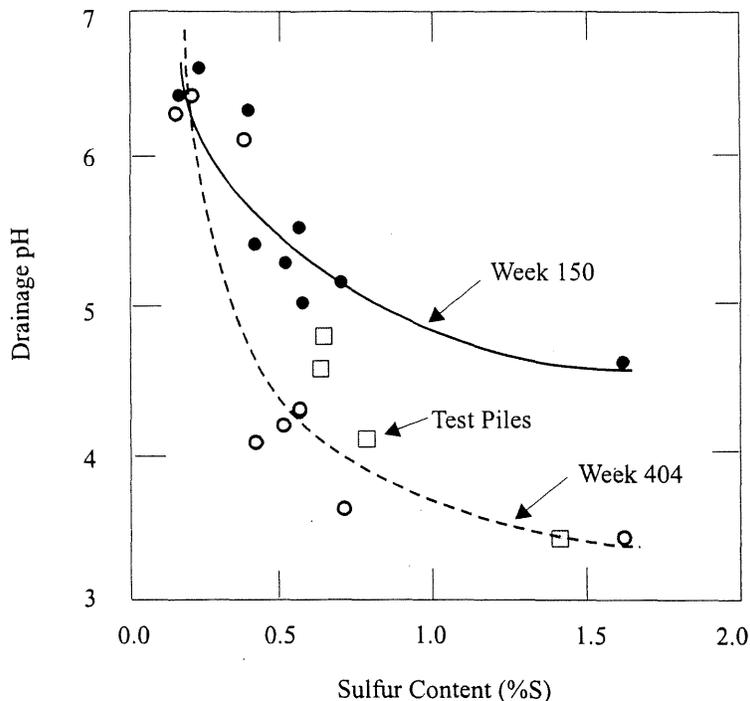


Figure 5. The minimum drainage pH of the blast hole solids in the laboratory were consistent with observed values in the field (AMAX test piles).

### 3.2.4. Comparison of field and laboratory data on Duluth Complex rock.

A similar trend in drainage pH with respect to time and sulfur content was observed in both the laboratory after 78 and 150 weeks, and field test piles experiments over 16 years (Lapakko 1994a). The ultimate drainage pH values for the 0.63% sulfur test piles was similar to values observed in the laboratory. However, minimum pH values for higher sulfur content test piles were about one unit lower than the corresponding laboratory values for these sulfur contents (figure 5). The rates of sulfate, calcium, and magnesium release in the laboratory were 3 to 10 times higher than those for the test piles.

The lower field rates may be due to several factors. First, field rates of sulfide mineral oxidation may be slower due to differences in the sulfide mineral surface area available for reaction. Since the iron sulfide mineral oxidation produces the acid which drives silicate mineral dissolution, lower release of calcium and magnesium in the field would be expected due to the lower sulfate release. Second, cooler temperatures in the field, and possibly lower oxygen concentrations (although oxygen transport is not likely limiting in the small piles), would retard oxidation. Third, lower field release may be due to limited transport of reaction products due to chemical precipitation at the higher field concentrations or the limited water available to transport reaction products from the piles.

The observation of field pH values lower than laboratory values at the higher sulfur contents was puzzling. Considering the decrease of pH with decreasing particle size observed in the laboratory (Lapakko et al. 1995), drainage pH from the larger field particles would be expected to exceed that from the small laboratory particles. Continued laboratory testing shed light on this apparent contradiction, revealing that the pH of drainage from samples with sulfur contents exceeding 0.40 percent continued to decrease (see also the laboratory section on blast holes at the Dunka site). After 404 weeks of dissolution in the laboratory, the higher sulfur content samples generally approximated field pH values (MN DNR 1997, unpublished data). In contrast, the pH values for the lower sulfur content samples in the laboratory were typically a unit lower than those in the field. This is consistent with the particle size dependence of drainage pH observed in laboratory experiments.

However, given the laboratory-field agreement for drainage pH from the higher sulfur solids, it may also suggest that pH of drainage from the 0.63 percent sulfur field piles would have continued to decrease had the piles not been dismantled. A visually estimated relationship between pH and time was graphed for the low sulfur field piles, which suggested that drainage pH values asymptotically approach a minimum value in the range of 4.6 to 4.8. The 404 week dissolution pH values observed in the laboratory are in better agreement with the estimated minimum drainage pH values for the low sulfur field piles (figure 5).

Drainage pH values in the circumneutral range associated with the low-sulfur gabbro at dimension stone quarries (pH 6.5 to 6.8 for sulfur contents less than 0.05%; Lapakko and Oberhelman 1993) are also semiquantitatively consistent with the observed dependence of laboratory drainage pH on sulfur content. Correlation of field data from the Dunka site to laboratory data was tenuous due to uncertainties in field pile composition. The lowest pH at the site, 4.2, was associated with a stockpile reported to contain only 0.24 percent sulfur. Higher sulfur content rock at the site produced higher drainage pH values. It is assumed that the lack of correlation between sulfur content and drainage pH at the site is the result of inadequate data on stockpile composition and/or the presence of relatively small amounts of highly reactive mineralized Virginia formation hornfels in some piles. The presence of this rock could depress drainage pH even when present in small amounts.

### **3.3. Drainage quality from greenstone belt gold mine tailings and waste rock.**

Although no gold mines have been developed in greenstone belts in Minnesota, these areas are being explored for their mineral potential due to the successful development of gold resources in this formation in southern Canada. To investigate the quality of drainage from such wastes, tailings samples for kinetic testing experiments were collected from active gold mines in greenstone belts and also from sulfide bearing waste rock generated during non-mining related excavation within the abandoned Soudan iron mine in Soudan, MN.

### 3.3.1. Tailings.

The ten tailings samples (T1-T10) from operating North American gold mines were compositionally characterized (particle size, chemistry, mineralogy) and subjected to dissolution testing to examine the relationship between the solid phase characteristics and drainage quality (Lapakko 1991a, Lapakko et al. 1999). The tailings were quite fine, with roughly 50 to 100% in the minus 270 mesh size fraction. They contained 0.1% to 7.6% sulfur, most of which was associated with pyrite and pyrrhotite, and a total calcium carbonate and magnesium carbonate mineral content of 1.4% to 21%. Sulfide and carbonate mineral liberation generally exceeded 90 percent. The neutralization potential (NP) determined by the method of Sobek et al. (1978) typically exceeded the total calcium carbonate and magnesium carbonate content, while the NP determined by the method of Lawrence (1990) more closely approximated this value (Lapakko and Wessels 1993, 1994; Lapakko 1993c).

None of the samples produced acidic drainage during the initial 52-week dissolution experiment, despite oxidation of iron sulfide minerals present in the tailings (Lapakko 1991a). Dissolution testing of four of these samples was continued (Lapakko et al. 1999; Lapakko and Wessels 1994, 1995; Lapakko 1993c). One of these samples (T9) produced circumneutral drainage for 120 weeks, and at week 121 the drainage pH dropped below 6.0, eventually reaching pH 3.45 at week 151 (Lapakko 1993c). The pH of drainage from samples T6, T10 and T2 decreased below 6.0 at weeks 284, 429 and 587, respectively. These examples demonstrate that the quality of drainage generated in short term dissolution experiments may not accurately reflect the drainage quality generated by mine wastes over a longer time frame. The comparison of oxidation rates with solid phase sulfur contents indicated that no solid-phase variables other than pyrite surface area were controlling rates of iron sulfide oxidation in this experiment (Lapakko and Wessels 1994, 1995; Lapakko 1993c).

Barium, zinc, arsenic, antimony, and molybdenum were the most commonly released trace metals. The laboratory data provided a good indication of potential for trace metal release in the field. Particularly for arsenic, molybdenum and zinc. Barium concentrations in mine waste drainage in the field, where sulfate concentrations are typically high, would probably be controlled by the limited solubility of barium sulfate. Arsenic, antimony, and molybdenum, when occurring in elevated concentrations as sulfide minerals, may produce elevated concentrations even if drainage is neutral (Lapakko and Wessels 1994; Lapakko 1993c).

In addition to dissolution testing at room temperature, six of these samples were subjected to dissolution testing at 100°C (T1, T2, T4, T8, T9, T10). At the higher temperature, samples T9, T2 and T10 produced acidic drainage after 8, 60 and 217 weeks, respectively (Lapakko 1993c). In contrast, the lag times at room temperature were 121, 587 and 429 weeks (MN DNR Hibbing Laboratory 2001, unpublished data). Dissolution tests at elevated temperatures may predict the quality of drainage from mine wastes much more rapidly than dissolution tests at lower temperatures. However, erratic pH variations often observed in these tests were difficult to interpret, and cast doubt on the reliability of predictions based on these tests. Reaction temperatures well above those observed in the field cast further doubt on the predictive accuracy of this test.

### **3.3.2. Waste rock.**

Recently, sulfide bearing waste rock samples were collected during non-mining related excavation of a cavern in Archean greenstone formations near Soudan, MN. Samples were extensively characterized and then subjected to laboratory dissolution testing to determine the relationship between sulfur content and drainage quality. Four field piles of variable sulfur content were also constructed to aid extrapolation of laboratory results to operational conditions.

Drainage pH values from the laboratory experiments reflected the balance of acid producing and acid neutralizing reactions taking place (Antonson and Lapakko 2000; Lapakko and Antonson 2001; Lapakko et al. 2001). Samples containing less than or equal to 0.16% sulfur yielded drainage pH values above 6.2 while those containing between 0.2 and 0.5% sulfur yielded minimum pH values from 4.0 to 4.4. Samples containing 0.59 to 1.22% sulfur yielded pH values as low as 3.1. Neutralization by the small amounts of calcium and magnesium carbonates was short lived in these rocks, and the reaction rates of silicate minerals (chlorite and sericite) was apparently inadequate to neutralize the acid when sulfur contents exceeded 0.16%. A sample containing 0.72% sulfur did maintain drainage pH greater than 6.0 due to the presence of magnesium, and to a lesser extent calcium, in siderite in the sample. Significantly, pyrite oxidation rates in the experiments were estimated to be close to literature values.

The four field piles, containing 0.02, 0.20, 0.39, and 0.67% sulfur respectively, were yielding significant concentrations of sulfate, but drainage pH values fell between 7.3 and 8.1. Oxygen content of gas within the piles generally ranged from 15 to 20% but several values of 8 to 9% were recorded. It is believed that some readings were spurious and the oxygen content in the pile virtually equalled that in the atmosphere.

### **3.4. Siltite-argillite waste rock drainage quality.**

Twenty one siltite-argillite samples were subjected to compositional characterization and dissolution testing to determine drainage quality for a specific lithology (Lapakko 1996, 1998a, 1999b). Data from these dissolution experiments will be used by the US Bureau of Land Management to develop a mathematical model to describe the dissolution of various rock types. Relative to the MN DNR small reactor studies, all samples were coarse (100% passing 1/4 inch vs -100/+270 mesh) and were subjected to accelerated weathering tests conducted according to ASTM Standard Method 5744-96. Sulfur content of the samples ranged from 0.12 to 5.7 percent.

Sulfur in nine of the samples was present almost entirely as sulfate, while the sulfide content in the remaining 12 samples ranged from 0.14 to 5.75 percent. Rocks in which sulfur was present largely as sulfate exhibited sulfate release which was less than or equal to that from rocks in which substantial sulfide was present. The sulfate release from the former group was due to slow dissolution of alunite and jarosite, as well as oxidation of trace amounts of iron sulfide. Iron sulfide oxidation released the majority of sulfate from the latter group.

Based on solid-phase sulfur speciation and sulfate release rates, four groups of rocks were identified: 1) sulfate rock with low sulfate release; 2) sulfate rock with high sulfate release; 3) sulfide rock with low sulfate release; and 4) sulfide rock with high sulfate release. In addition to sulfate release, characteristic ranges of calcium and magnesium release and drainage pH values were determined for each group. Extensive chemical analysis was conducted on all samples, and one or two samples from each of the four groups was subjected to intensive mineralogic analysis. Other than solid-phase sulfur speciation (sulfate rock vs sulfide rock), no solid-phase variables were identified as strongly influencing the rate of sulfate release.

The weathering history of the rock in the field may have played a dominant role in the dissolution behavior of the rocks. In particular, high sulfate release was observed for rocks on which acidic reaction products had accumulated due to leaching in the environment. Similarly, sulfide rocks containing substantial carbonate minerals tended to have lower sulfate release rates due partly to the pH elevation resulting from carbonate mineral dissolution.

### **3.5. Mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks.**

Eleven waste rock samples were extensively analyzed and then subjected to accelerated weathering experiments using the ASTM standard method D-5744-96 and MN-DNR modified methods (see 4.3.4; Lapakko 1998c, 1999c; Lapakko and Antonson 2000b). These included seven mafic-intrusive rocks, three tuffaceous-sedimentary, and one weathered carbonate-hosted waste rock sample from an old mine dump. Sulfide contents in the mafic-intrusive and tuffaceous-sedimentary rocks ranged from 6 to 9 percent and 1.3 to 3.75 percent, respectively. These rocks all contained significant amounts calcium and magnesium carbonate and so would likely not become acidic for some time. Only one of the samples had a neutralization potential that was greater than the acid producing potential. The weathered waste rock sample had a sulfide content of 11.5 percent. Some magnesium carbonate and lesser calcium carbonate were present in the siderite in this sample.

#### **4. EVALUATION OF PREDICTIVE TESTS.**

Several static and kinetic tests have been developed for predicting mine waste drainage quality. Static tests base predictions on solid phase analyses, while kinetic tests use data from dissolution tests on mine waste samples. Insight into static and kinetic test accuracy and interpretation has been gained as part of MN DNR testing of Duluth Complex rock and hydrothermal quartz-carbonate gold tailings. The influence of protocol variables was also examined as part of the latter research, which was funded by the Minnesota Minerals Coordinating Committee and MN DNR Division of Minerals (Lapakko 1991a). To evaluate several static and kinetic tests on a compositional range of mine wastes, the U.S. Environmental Protection Agency provided funding to the MN DNR for a project which was administered by the Western Governor's Association (WGA). A literature review was produced and followed by empirical evaluation of the ability of tests to predict mine waste drainage pH (Lapakko 1991b, 1992a). The EPA funded a project continuation, in which two dissolution tests were continued for a total duration of 132 weeks and the effect of particle size on mine waste drainage quality was examined (Lapakko et al. 1995).

##### **4.1. Overview of mine waste characterization techniques.**

Effective and efficient remediation of mine wastes requires tailoring remedial designs to the quality and quantity of drainage from mine wastes. While some mining wastes will require no remediation, others, some of which may appear to be environmentally benign today, will require some or even extensive remediation to effectively control mine drainage problems well into the future. A number of tools have been developed to help characterize mine wastes and to predict drainage quality and many are summarized by Lapakko (2001b). These include tools ranging from the screening of large areas of abandoned mine wastes to determining compositions of individual mineral grains.

##### **4.2. Evaluation of static tests.**

Static tests base drainage quality prediction on measurements of the maximum capacity of a mine waste to produce acid (Acid Production Potential or AP) and to neutralize acid (Neutralization Potential or NP). They do not account for the availability of the neutralizing minerals or the rate at which they dissolve. AP is based on the quantities of sulfur present as acid-producing sulfide and sulfate minerals. Since techniques for determining these quantities have been developed and applied for geological assessment over many years, they are fairly accurate. In research on Duluth Complex rock, hydrothermal quartz-carbonate tailings, and the WGA/EPA studies it was determined that static tests tend to generally overestimate NP, and that the extent of overestimation is dependent on the sample mineralogy. In particular, the presence of calcium plagioclase and iron carbonate minerals tends to increase the extent of overestimation. Additional summary information on static tests is presented in White et al. (1997, 1999).

#### 4.2.1. Assessing neutralization potential accuracy.

The MN DNR has applied four methods for assessing the accuracy of static test NP measurements. The first is based solely on solid-phase analysis, while the remaining three require dissolution testing and account for the availability of neutralizing minerals and their rate of dissolution. First, with samples for which there are no empirical dissolution data, NP accuracy can be assessed by comparison with the neutralization present as calcium and magnesium carbonate minerals in the sample (NP[(Ca/Mg)CO<sub>3</sub>]) expressed in units of mg CaCO<sub>3</sub>/ g rock (equation 18).

$$\text{NP}[(\text{Ca/Mg})\text{CO}_3] = (10 \times \% \text{CaCO}_3) + (11.9 \times \% \text{MgCO}_3) \quad (18)$$

This approach assumes that these carbonate minerals are the only neutralizing minerals present (Lapakko 1991a, 1992b, 1994b).

Second, with samples which have been subjected to dissolution tests and produced acidic drainage, the laboratory empirical NP (ENP, expressed as mg CaCO<sub>3</sub>/ g rock) of the sample can be determined based on the observed sulfate (equation 19) or major cation (Ca, Mg, equation 20) release prior to acidification (Lapakko 1990a, Lapakko and Wessels 1995).

$$\text{ENP}(\text{SO}_4) = 1.04 \times \sum \text{SO}_4 / \text{g rock} \quad (19)$$

$$\text{ENP}(\text{Ca}+\text{Mg}) = (2.50 \times \sum \text{Ca} + 4.12 \times \sum \text{Mg}) / \text{g rock} \quad (20)$$

where  $\sum \text{SO}_4$ ,  $\sum \text{Ca}$ , and  $\sum \text{Mg}$  represent the cumulative mass, in mg, of sulfate, calcium and magnesium, respectively, released at the time at which the drainage pH dropped below 6.0.

For these experiments the amount of sodium and potassium, which could represent neutralizing reactions, was assumed to be negligible. The cumulative masses of sulfate and major cations represent the amount of iron sulfide oxidation and the extent of calcium and magnesium carbonate mineral dissolution, respectively, prior to drainage acidification.

Third, for the aforementioned case, NP tests can be conducted on leached samples which produced acidic drainage during dissolution tests (Lapakko 1990a). Since the NP of these solids should be zero, any measured NP is an erroneous contribution of "false NP". Fourth, for samples which have produced acidic drainage in the field, a field ENP can be determined using the approach described above for the laboratory ENP (Lapakko 1994a). While these field data on the dissolution of well-characterized mine wastes provide the best quantification of capacity to neutralize acid, these data are unfortunately rare.

A number of experiments have been conducted to identify sources of error in neutralization potential determinations. Experiments conducted by the MN DNR and US Bureau of Mines have been summarized in several publications (White et al. 1997, 1999; Lapakko 1993d, 1994b, 1999d).

Neutralization potential was found to be most strongly influenced by differences in particle size, amount of acid added, back titration end-point, and, of course, sample mineralogy. Acid type and temperature of the digestion had little, if any, effect on neutralization potential determinations.

#### **4.2.2. Duluth Complex rock.**

Standard ABA NP values overestimate the capacity for Duluth Complex rock to neutralize acid while maintaining an environmentally acceptable pH. Although carbonate minerals are generally absent or are present at very low concentrations in Duluth Complex rock (Stevenson et al. 1979, Lapakko 1988a), Standard Acid Base Accounting (Standard ABA) NP values in the typical range of 10 to 20 kg/t CaCO<sub>3</sub> (inferring 1-2% CaCO<sub>3</sub>; Lapakko 1993a, White et al. 1997b) and as high as 33 kg/t CaCO<sub>3</sub> (Lapakko 1993d, 1994b) have been reported. Laboratory empirical NP values ranged from 0 to 2.0 kg/t CaCO<sub>3</sub> (Lapakko 1990a, 1993a, Lapakko and Antonson 1991, White et al. 1997a), confirming that the Standard ABA NP values overestimated (by 5 to 21 kg/t CaCO<sub>3</sub>) the capacity of this rock to neutralize acid while maintaining drainage pH above 6.0. Furthermore, even after the pH of effluent from the rock samples had decreased below pH 6, Standard ABA tests conducted on the leached solids indicated a residual NP, typically in the range of 8 to 14 kg/t CaCO<sub>3</sub> (White et al. 1997a). Based on data from field test piles of Duluth Complex rock, the field ENP was determined to range from 0.04 to 1.3 kg/t CaCO<sub>3</sub> and, as was the case for laboratory values, tended to decrease as sulfur content increased (Lapakko 1994b).

#### **4.2.3. Hydrothermal quartz-carbonate gold tailings.**

For hydrothermal quartz-carbonate hosted gold mine tailings, the AP and NP determined by the Modified Acid Base Accounting (Modified ABA) were more accurate than the corresponding values determined by Standard ABA (Lapakko 1991a, 1992b). The AP determinations were slightly more accurate since they excluded small amounts of sulfur present in non-acid producing sulfate in the samples. The NP values more closely approximated the total calcium carbonate and magnesium carbonate content of the tailings.

Two samples for which the Modified ABA overestimated the total calcium and magnesium carbonate content of the tailings by 40%, had the highest siderite content of the samples examined. Standard ABA NP values were elevated by "false NP" contributed by feldspar, chlorite, and/or mica present in all samples. Such contributions were particularly high for samples containing larger amounts of siderite, feldspar, and mica. Examination of static test method variables indicated that, relative to the Modified ABA, the lower digestion pH and backtitration endpoint pH of the Standard ABA contributed to the elevated NP values.

Two samples produced acidic drainage during laboratory dissolution tests at ambient temperature. Standard and Modified ABA NP values were within 12.5 percent of the ENP of one sample (T9, Lapakko and Wessels 1995) but overestimated this value by 65 to 70 percent in a second (T6, MN DNR, unpublished data). The NP[(Ca/Mg)CO<sub>3</sub>] was within 12.5 percent of the ENP for both

samples. As a sidelight, it is interesting to note that the ENP at ambient temperature was higher than that observed in kinetic tests at elevated temperature. This suggests a difference in the carbonate mineral dissolution in the two tests which must be considered in comparisons of NP and ENP.

#### **4.2.4. Several NP tests on a variety of samples.**

In the WGA/EPA project, ten mine waste samples of variable composition were subjected to Standard ABA, Modified ABA, and B.C. Research Initial tests to evaluate the tests' ability to predict mine waste drainage pH (Lapakko 1993d, 1994b). It was concluded that the AP could be accurately quantified, and that the tests tended to overestimate the ability of mine wastes to neutralize acid while maintaining a neutral pH. The presence of iron carbonates, calcium feldspar, and possibly olivine and pyroxenes in the mine waste tended to increase the extent of overestimation.

A modification of the Net Acid Production Test compared favorably with the Net NP (NP-AP) values of the aforementioned static tests (Lapakko and Lawrence 1994). In order to address the problem of overestimating the NP of a rock sample, an alternative technique that determines the NP available to maintain a drainage pH of 6.0 or greater was proposed (Lapakko 1994b). NP determinations using this technique approximated the neutralization potential available as calcium and magnesium carbonate within 3 kg/t CaCO<sub>3</sub>, suggesting that the desired quantification was reasonably accurate.

### **4.3. Evaluation of kinetic tests.**

#### **4.3.1. Assessing kinetic test accuracy.**

To truly assess the accuracy of kinetic test results they must be compared, perhaps after modeling, to long-term field results for the same mine waste. While laboratory drainage pH from Duluth Complex rock agreed well with field data (Lapakko 1994a, see also section 3.2.4), data for such comparisons are rarely available. Consequently, it is rarely possible to assess kinetic test accuracy based on field verification, and the extent to which the laboratory tests model field behavior must be addressed conceptually.

Kinetic tests involve dissolution of mine waste samples, for periods typically on the order of 20 to 40 weeks, and analysis of the resultant water quality. Tests such as these permit identification of some acid-producing mine wastes based on the laboratory drainage pH. However, if the mine waste contains a moderate amount of neutralization potential, it may not be depleted during the course of the test and drainage will remain neutral. Based on such data it might be concluded that the solids were not acid producing. However, over a longer duration the NP may be depleted while iron sulfides remain and continue to oxidize. In such a case the drainage would acidify upon depletion of the neutralizing minerals. Thus, to determine the degree to which laboratory tests model long-term field behavior, it is necessary to determine the extent to which acid producing and acid neutralizing minerals have been depleted in kinetic tests.

### **4.3.2. Comparison of kinetic tests.**

In the WGA/EPA study (Lapakko 1993d) four waste rock and six tailings samples were subjected to six kinetic tests (Wet-Dry Cycle, Standard Humidity Cell, Modified Humidity Cell, Elevated Temperature, Soxhlet, Shake Flask tests). All tests simulated the acidic field drainage pH from a sample with a reasonably high sulfur content and an NP near zero. With the remaining samples, the Modified Humidity Cell and Elevated Temperature Tests most closely simulated the available verification data. The Modified Humidity Cell Test was conducted only on waste rock samples, and its accuracy was attributed to the larger particle size used in the test. The larger particle size more closely simulated the availability of iron sulfide and calcium/magnesium carbonate minerals in field scale waste. The accuracy of the Elevated Temperature Test was due to the acceleration of sulfide oxidation, typically 1.5 to 4 times that observed in other tests, and the attendant acid production.

For most samples, less than ten percent of the sulfide present was oxidized during the 20-week tests (though three of the nine samples in the Elevated Temperature Test had between 10 and 30% of their sulfide oxidized). Consequently, the samples retained a substantial capacity to produce acid. After 20 weeks of dissolution, the sulfide oxidation and attendant acid production during most tests was not adequate to overcome the acid neutralization potential available in samples with a moderate amount of calcium and/or magnesium carbonates. The remnant AP generally exceeded the remnant NP, suggesting that drainage may eventually acidify (Lapakko 1990a; Lapakko and Antonson 1991).

Due to the potential for eventual acidification of drainage, the US EPA funded additional Wet-Dry Cycle and Elevated Temperature testing on the ten mine waste samples from the WGA/EPA project. By the end of 132 weeks, none of the samples that had produced neutral drainage in the initial testing had acidified despite apparent depletion of calcium and magnesium carbonate minerals while iron sulfide minerals remained and oxidized (Lapakko et al. 1995). Subsequently, five samples (RK4, TL2, TL3, TL4, TL6) have acidified in the Wet-Dry Cycle Test, three of which acidified after 200 weeks (MN DNR Hibbing Laboratory 1997, unpublished data). In the Elevated Temperature Test, five samples (RK3, RK4, TL2, TL4, TL6) acidified by week 163, and two samples produced drainage with a pH of approximately 6.0 (Lapakko et al. 1995).

### **4.3.3. Influence of kinetic test protocol variables.**

#### **4.3.3.1. Effect of test duration.**

In the WGA/EPA project and testing of hydrothermal quartz-carbonate gold tailings (Lapakko 1993c; Lapakko and Wessels 1995; see also section 3.3), there were 12 cases in which drainage pH fell below 6.0 after 53 to 284 weeks of dissolution testing (table 1). Predictions based solely on kinetic

Table 1. Summary of solids that have acidified during prolonged kinetic testing.

Solid	Test	Week of Acid.	NP [(Ca/Mg) CO <sub>3</sub> ]	ENP (Ca/Mg)	% S <sup>2-</sup>	Original AP	AP Released	AP Remaining	% AP Released
RK1	Elev-Temp	240	3	10	0.42	18	10	8	57
RK2	Elev-Temp	168	2	5	0.63	26	3	23	11
RK3	Elev-Temp	20	5	5	1.60	67	6	61	9
RK4	Wet-Dry	167	32	22	2.82	118	17	101	14
	Elev-Temp	16	32	27	2.82	118	22	96	19
TL1	Elev-Temp	223	19	24	0.90	38	14	24	37
TL2	Wet-Dry	233	16	26	1.22 <sup>1</sup>	51	9	42	18
	Elev-Temp	53	16	21	1.22 <sup>1</sup>	51	12	39	24
TL3	Wet-Dry	258	19	41	1.81 <sup>2</sup>	75	19	56	25
	Elev-Temp	271	19	44	1.81 <sup>2</sup>	75	15	60	20
TL4	Wet-Dry	192	6	8	2.10	88	5	83	6
	Elev-Temp	57	6	6	2.10	88	4	84	5
TL6	Wet-Dry	256	46	82	5.26 <sup>3</sup>	219	57	162	26
	Elev-Temp	163	46	81	5.26 <sup>3</sup>	219	54	165	25
T2	Elev-Temp	62	189	154	7.30 <sup>4</sup>	304	172	132	57
T6	Wet-Dry	284	45	40	2.07 <sup>4</sup>	86	23	63	27
T9	Wet-Dry	122	14	16	3.64 <sup>4</sup>	152	10	142	7
T10	Elev-Temp	217	201	159	5.93 <sup>5</sup>	247	147	100	60

Note: All values are mg CaCO<sub>3</sub>/g rock

1=average of sulfide analyses (1.45, 0.90, 1.31)

2=average of sulfide analyses (2.12, 1.49)

3=average of sulfide analyses (5.18, 5.34)

4=Bondar-Clegg analysis from 6/13/90, non-Fe report

5=average of 6.3, 5.4, and 6.09 %S<sup>2-</sup> analyses

test drainage quality over the common 40-week duration would erroneously identify these solids as non-acid producing. These solids clearly had no NP remaining to maintain environmentally acceptable drainage pH values. Remnant AP ranged from 35 to 147 mg CaCO<sub>3</sub>/g, indicating samples could continue producing acid for a considerable time (table 1). Thus, drainage quality in short-term tests may not simulate the long-term drainage quality from mine wastes in the field. However, tests of extended duration may delay the mine permitting process beyond a practical time frame prior to mine development. These results further underline the importance of considering the solid phase characteristics of samples, particularly iron sulfide and calcium and magnesium carbonate content, when designing kinetic tests and interpreting their results.

To address this problem, Lapakko (1990a) developed a method to estimate the dissolution time required to deplete NP, or “lag time”, based on the carbonate mineralogy and calcium and magnesium release rates. This method of estimation assumes that all carbonate minerals, and only these minerals, will neutralize acid. However, it ignores the formation of precipitate coatings on acid producing and acid neutralizing minerals, which inhibit mineral dissolution. The method was reasonably accurate for mixtures of sulfidic rock and alkaline solids.

Kinetic testing of the hydrothermal quartz-carbonate gold mine tailings (see section 4.2.3) revealed two samples with long lag-times in the Wet-Dry Cycle Test at room temperature. One of these samples (T9) acidified after 122 weeks (Lapakko 1993c; Lapakko and Wessels 1995) and the other (T6) after 284 weeks (MN DNR Hibbing Laboratory 1997, unpublished data). Calculations using the method of Lapakko (1990a, see second paragraph of section 4.2.1) indicated that these samples would acidify after weeks 112 (Lapakko 1993c; Lapakko and Wessels 1995) and 322, respectively, which was in reasonable agreement with the observed values. This method will be used to calculate the time to drainage acidification for all solids with long lag times.

#### **4.3.3.2. Effect of particle size.**

To determine the effects of particle size on drainage quality, each of the three rock types were separated into six different size fractions, and subjected to dissolution testing (Lapakko et al. 1995, 1998). The effects of rock particle size on drainage pH were variable. The fine fraction of one rock type produced the lowest drainage pH, while the largest size fraction produced the lowest drainage pH for a second rock type. With a third rock type there was little effect of particle size on drainage quality. The effect for a particular rock type was apparently due to the influence of particle size on the relative abundance of iron sulfide and carbonate mineral surface areas.

#### **4.3.3.3. Effect of sample mass and rinse interval.**

The mass of mine waste used in laboratory predictive tests affects the extent of acid neutralization by dissolution of calcium and magnesium carbonate minerals (Lapakko 1993c). Using too small of a mass may underestimate the ability of a mine waste to neutralize acid. The same study indicated the rinse interval used in laboratory tests had only a slight influence on drainage quality.

#### **4.3.4. Evaluation of ASTM Modified Humidity Cell method.**

More recently, the MN DNR conducted further Modified Humidity Cell dissolution testing using ASTM Standard Method 57744-96 on the eight gabbroic samples from the Duluth Complex and five from siltite argillite rocks. As part of the ASTM evaluation procedure, these results were compared with those from other laboratories using the same method on the same samples (Lapakko 1996, 1998b; Lapakko 1999a; Lapakko and Antonson 2000; White and Lapakko 2000). Experiments performed in different labs for the two types of rocks agreed reasonably well with each other. Differences in pH during gabbro experiments were generally within 0.1 pH units, but ranged up to 0.4, and the release rates for sulfate, calcium, and magnesium, typically agreed within 10%. Results from experiments involving the siltite-argillite rock also compared reasonably well between laboratories, with the exception of one sample which exhibited drainage varying between labs by as much as one pH unit.

The MN DNR also subjected the same sample to dissolution testing using three simplified modifications of the ASTM Standard Method (Lapakko and White 2000). Mine waste drainage quality predictive tests using these modifications could be conducted at lower cost than with the ASTM Method 5744-96. Sulfate and calcium release rates were generally similar, but the MN DNR technique typically produced drainage with higher Mg release. Final drainage pH, however, agreed to within 0.1 pH units for six of the nine samples tested and were within 0.4 pH units for the other three.

## **5. MITIGATION TECHNIQUES.**

The degree of mitigation required for mining wastes depends directly upon the potential for problematic mine waste drainage quality at a site. Appropriate methods of mitigation can be designed and optimized based, in part, upon the predicted drainage quality. The MN DNR Division of Lands and Minerals has studied both passive and active mitigation techniques in the laboratory and on an operational scale. Results from these studies are presented below.

### **5.1. Literature Reviews.**

Extensive literature exists on the subject of mitigation techniques. The MN DNR has compiled and summarized the current state of environmental mine waste technology, specifically as it relates to present and possible future ore deposits located in Minnesota. Fifteen environmental mine waste strategies were identified, which could be subdivided into three separate categories: those focused on prevention, control and treatment of problematic mine waste drainages (Jakel and Lapakko 1999f; Leopold and Lapakko 2000, 2001d).

### **5.2. Operational scale mitigation.**

The second phase of an experimental program funded by the U.S. Bureau of Mines was also conducted at the AMAX/Kennecott site. This two-phase program examined the feasibility of removing trace metals (Cu, Ni, Co, Zn) from stockpile drainage using readily available materials (peat, till, wood chips, Cu-Ni tailings, zeolite) in low-cost, low maintenance systems. The results of the entire program are presented in two reports (Lapakko et al. 1986a, 1986b), and synopses of various research segments are presented in several symposium proceedings (Eger et al. 1984; Lapakko and Eger 1988, 1983, 1981a; Lapakko et al. 1983).

Passive and active mitigation techniques have been applied to stockpiles and stockpile seepages at the Dunka Mine (Figure 6) to prevent, control, and treat known and potential water quality problems (LTV Steel Mining Company 1996). Prevention methods include stockpile capping, diversion ditches, and moving rock off site (STS Consultants Ltd. 1993, 1994a, 1994b). Stockpile capping techniques were selected based on the stockpile drainage quality and chemical composition. Stockpiles with no known water quality problems and relatively low sulfur contents were capped using standard mineland reclamation (two feet of overburden). Stockpiles with known water quality problems or elevated sulfur contents were capped with either enhanced mineland reclamation (two feet of minus 6-inch uncompacted material with at least 10% in the -200-mesh fraction: stockpiles 8011, 8031, and 8012); enhanced mineland reclamation with linear low density polyethylene (LLDPE) membrane lined ditches (stockpiles 8013 and 8014); or covered with a LLDPE membrane liner (8018 and the hornfels pile on the 8014) (STS Consultants Ltd. 1994a).

Diversion ditches to reduce surface and ground water input to stockpiles were constructed on the west side of the 8014 draining to the pit; the west side of the 8013 draining to the pit; a bedrock cut

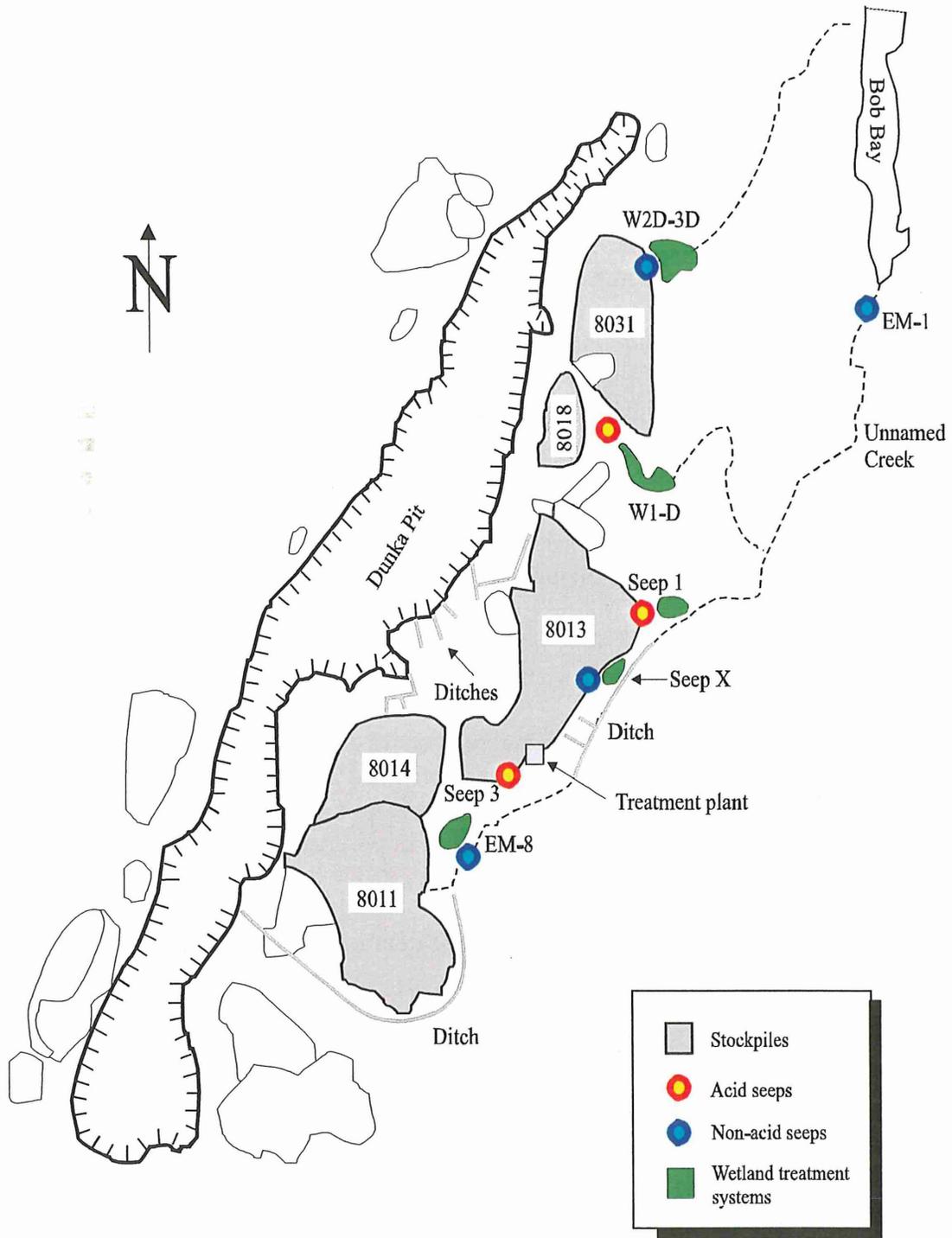


Figure 6. Map depicting passive and active mitigation at the Dunka Mine.

in Unnamed Creek east of Seep 1 to lower the water table at the toe of the 8013 stockpile; from the Environmental Sump to the pit; on the south side to the 8011 draining into the Environmental Sump and subsequently into the pit; and to redefine the east 8011 drainage ditch.

A mass of 262,652 long tons of mineralized Virginia Formation hornfels rock was moved off site to LTV's tailings basin. The rock was mixed with 31,468 tons of dolomitic limestone (to neutralize acid) and buried in the tailings to inhibit oxygen transport to the rock and consequent oxidation of the sulfide minerals present. The tailings also contained ankerite for additional neutralization potential and iron oxyhydroxide minerals as potential trace metal adsorbing surfaces.

To inhibit potential decreases in drainage pH, limestone was added to high sulfur rock on the 8014 and 8031 stockpiles (LTV Steel Mining Company 1996; Dewar 1996). Treatment methods at Dunka include passive wetland treatment systems (Eger 1992; Eger et al. 1996, 1997, 1998) and an active treatment plant (STS Consultants Ltd. 1994b). Constructed wetland treatment systems include limestone/peat systems at seeps W2D/W3D (061) and Seep X (044), a limestone pretreatment followed by a limestone/peat system at W1D (051), and a limestone pretreatment followed by a peat system at Seep 1 (043). A limestone/peat system was constructed in 1998 for EM8 (041). The active treatment plant is a lime precipitation system designed to treat flow from EM8, Seep 1, Seep X, and W1D treatment systems.

### **5.3. Blending alkaline solids with mine waste.**

The addition of alkaline solids to acid-producing mine waste may provide 1) short-term mitigation by neutralizing acid produced by iron sulfide oxidation and 2) long-term mitigation by facilitating the passivation of iron sulfide mineral surfaces. Laboratory experiments blending Duluth Complex with rotary kiln fines and with limestone have been in progress since 1988. Field tests blending Archean greenstone with limestone were initiated on 24 October 2000.

#### **5.3.1. Laboratory experiment with Duluth Complex rock**

In a laboratory experiment which began in May 1988, rotary kiln fines (RK fines; a waste product generated by the conversion of limestone to lime), -10 mesh limestone, and +10 mesh/-0.25 inch limestone were each mixed with finely-crushed Duluth Complex rock ( $0.053 < d \leq 0.149$  mm) to examine their effectiveness in reducing the release of acid and trace metals in drainage from the rock. The finely-crushed Duluth Complex rock, simulating tailings or fine waste rock, contained 2.1 percent sulfur and the predominant iron sulfide mineral was pyrrhotite. The calcium content of the RK fines indicated a combined calcium carbonate/oxide content of 63 percent, while the combined calcium and magnesium carbonate (96.7% and 2.1%, respectively) content of the limestone was 99.1 percent as  $\text{CaCO}_3$ .

In addition to duplicate control reactors, five loadings (0.5, 1.0, 2.0, 3.0, and 5.0 g alkaline solid/g sulfur in rock) of each solid were mixed with 75 g Duluth Complex rock. Duplicate reactors were

used for the 1.0 and 3.0 g loadings. This produced neutralization potential to acid production potential quotients (NP/AP) of 0.11 to 1.1 for the RK fines and 0.16 to 1.6 for the limestone. The mixtures were subjected to a "wet-dry cycle" laboratory test, which is yet in progress. The following section summarizes the results of the experiment for the first 585 weeks. Additional detail on this study is available in three status reports (Lapakko and Antonson 1989a, 1990a; Lapakko et al. 1998a) and in three papers (Lapakko and Antonson 1991; Lapakko et al. 1997; Lapakko et al. 2000).

The pH of drainage from **the rock alone** decreased below 6.0, a common minimum water quality standard, after 8 weeks and reached a minimum of 3.3 in 117 weeks, at which time the controls were terminated. Maximum copper and nickel concentrations ranged from 1 to 2 ppm. The sulfate release did not decrease over time. The **minus 0.25-inch/+10 mesh limestone** treatment produced drainage similar to that of the controls and was discontinued after 40 weeks. In contrast, the RK fines and -10 mesh limestone maintained drainage pH above 6.0 for 75 to 585 (still in progress) weeks. While pH was in this range, sulfate concentrations decreased and trace metal concentrations were typically three to ten percent of those observed in drainage from the controls.

The **RK fines** elevated pH and inhibited sulfate release for time periods which increased with the mass of RK fines present. The pH of drainage from the 0.11 quotient (NP/AP) loading decreased below pH 6.0 after 75 weeks of dissolution and reached a minimum of 3.6 after 117 weeks, at which time the reactor was terminated. Drainage from the duplicate 0.22 quotient loadings of RK fines decreased below 6.0 after 95 and 170 weeks. The former was terminated after 117 weeks, and the latter (still in progress) reached a minimum pH of 2.8 after 512 weeks. Drainage pH from the 0.66 quotient decreased below 6.0 after 581 weeks. For the drainages that acidified, the cumulative calcium release indicated that 92 to 103 percent of the calcium carbonate/oxide initially present in the RK fines was dissolved at the time pH decreased below 6.0. Concentrations of nickel, cobalt, and zinc reached maximums after pH declined below 6.0, and copper concentrations tended to increase steadily as pH decreased. The pH of drainage from the 1.1 quotient, which remains operative, typically remained above 8.0 throughout the 585 week period of record.

Sulfate concentrations in the drainage generally declined until pH decreased below 6, and the highest values were observed after drainage acidification. With the 0.65 and 1.1 quotient loadings, drainage pH values were typically near 9.0, although after week 340 the pH of drainage from the 0.65 loadings began to oscillate occasionally into the sevens. Such oscillations preceded acidification of drainages from the 0.22 quotient loadings. Sulfate concentrations in the drainage from the 0.65 quotient loadings have decreased throughout the period of record. For each mixture, regression analysis for the equation  $[SO_4] = ae^{bt}$  was used to describe the decrease of sulfate concentrations (mg/L) with time (t, weeks) over the period during which pH remained above 6. The variables "a" and "b" are constants, and the values of b for the six cases ranged from -0.016 to -0.0031 (Lapakko et al. 1998a).

The **-10 mesh limestone** additions elevated drainage pH and net alkalinity while inhibiting sulfate release. The pH of drainage from the 0.16 quotient (NP/AP) loading was initially neutral, decreased below 6.0 after 109 weeks, reached a minimum of 5.0 at week 116, and subsequently increased to a typical range of 5.3 to 6.3 through week 709. This is in contrast to the pH from the lower loadings of RK fines, for which pH continued to decline after falling below 6.0. The lack of more extreme acidification was due to a decrease in the rate of sulfide oxidation by more than 80 percent. It is of interest to note that the sulfide oxidation rate did not increase after pH decreased below 6.0. Drainage pH from the higher limestone loadings remained above 6.0 and sulfate concentrations decreased with time.

As with the RK fines, regression analysis was used to describe the decrease of sulfate concentrations with time (see above), and the constant "b" for the seven cases ranged from -0.011 to -0.0066. The correlations for the fine limestone were considerably higher than those for the RK fines. All loadings reduced the sulfide mineral oxidation rates, and the loadings of 1:1 and greater reduced them to levels at which host rock silicate mineral dissolution would be adequate to neutralize the resultant acid production. Furthermore, the amount of silicate minerals present was large enough that their dissolution would neutralize the acid produced if the pyrrhotite present continued to oxidize slowly. The decline in sulfide oxidation may have been due to creation of a leached layer at the pyrrhotite

surface, pyrrhotite coating by products of precipitation reactions enhanced by the presence of the limestone, or cementation of pyrrhotite grains due to reactions within the bed.

This mitigative technique has excellent potential for neutralizing acid produced over a period of several years as an interim measure and promising potential for long term mitigation. However, certain precautions must be taken with the conclusions. First, the results are specific to the Duluth Complex mineralogy. For example, if sulfide minerals were coated by precipitates the coating composition, as well as mechanisms and rates of coating formation, may be specific to this rock formation. In addition, the dissolution of host rock minerals of other rock types are likely to provide different rates and capacities of acid neutralization than those of the Duluth Complex.

Second, these results were determined under laboratory conditions. The extent of limestone/mine waste mixing in the field is likely to be less complete than in the laboratory, and this extent is likely to influence the effectiveness of acid neutralization and sulfide mineral coating. In particular, it is difficult to obtain intimate contact when mixing relatively fine limestone with large waste rock particles. Environmental variables such as large fluctuations in temperature may also produce results deviant from those observed in the closely controlled laboratory environment. Of particular importance is determination of the longevity of the acid production inhibition.

### **5.3.2. Field test with Archean greenstone rock**

Field tests blending Archean greenstone rock with limestone were initiated 24 October 2000. Tests are being conducted in six polyethylene tanks (d = 48 in., h = 42 in.). The limestone additions were

made to attain approximate NP:AP ratios (neutralization potential:acid production potential) of 0:1, 1:1, and 3:1, with each mixture duplicated. Through the first year of the project, drainage pH values from all tanks have been in the range of 7.5 to 8.5. Although drainage pH values have demonstrated no obvious dependence on the treatment type, the most recent alkalinity values tended to increase with the amount of limestone present.

#### **5.4. Drainage treatment with limestone beds.**

##### **5.4.1. Laboratory tests.**

Column laboratory experiments to examine the ability of limestone beds to neutralize acidic stockpile drainage began in April 1988. Triplicate columns containing 780 grams of minus 0.25"/+10 mesh high calcium limestone were used to treat each of three different drainages. Flow rates were adjusted to maintain an effluent in which the alkalinity exceeded the acidity. Although the columns were successful in treating all three drainages, problems with plugging typically led to termination of columns. These problems occurred at different times and, consequently, periods of record for the columns varied.

For Seep 1, input flow was maintained at an average of 4.9 bv/d for most of the experiment, with total flow volumes ranging from 4200 to 5700 bed volumes. The mean input values for pH and net alkalinity were 5.6 and -22 mg/L as CaCO<sub>3</sub>. Limestone dissolution elevated these values to 7.5 and 20 mg/L as CaCO<sub>3</sub> in the column effluent.

For FL3, input flows averaged 0.15 bv/d, with total flow volumes ranging from 160 to 610 bv. The mean pH and net alkalinity were 4.9 and -210 mg/L as CaCO<sub>3</sub>. Dissolution of limestone elevated drainage pH and net alkalinity to approximate respective values of 7.9 and 75 mg/L as CaCO<sub>3</sub> in the column effluent.

For FL6, input flows averaged 0.51 bv/d, with total flow volumes of 550 to 990 bv. The mean input pH and net alkalinity were 4.1 and -580 mg/L as CaCO<sub>3</sub>. Dissolution of limestone elevated these values to respective means of 7.6 and 120 mg/L as CaCO<sub>3</sub> in the column effluent.

Copper concentrations were reduced by 85 to 98%. Nickel, cobalt and zinc concentrations were reduced to a lesser extent (Ni: 11-24%, Co: 7-22%, Zn: 35-65%). These results indicate that limestone beds are capable of neutralizing these stockpile drainages and substantially reducing copper concentrations if adequate detention time is allowed. Problems with maintaining flow, due to cementation of the bed, were encountered. Use of larger particles would reduce potential for such problems in the field but decrease the reactivity per mass limestone. Additional detail is available in status reports (Lapakko and Antonson 1989b, 1990a; Lapakko et al. 1998b) as well as a shorter technical publication (Lapakko and Antonson 1990d).

### 5.4.2. Field test.

A field scale limestone treatment bed (1.4 m<sup>3</sup> bed volume) began treating the Seep 1 drainage at the Dunka site on 26 September 1988 (Lapakko and Antonson 1989c). The objectives of this project were to:

- 1) elevate the pH and alkalinity while reducing the acidity and trace metal concentrations in the Seep 1 drainage;
- 2) describe the variation of treatment efficiency in terms of pH elevation and trace metal removal with the volume of drainage treated; and,
- 3) describe the variation of treatment efficiency as a function of detention time, or equivalently, flow rate.

The bed contained 2020 kg of high-calcium limestone (minus 6.4 mm), and was 1.3 m in diameter and 1 m deep. It received Seep 1 flow from 26 September to 28 October 1988, from 26 April until 31 October 1989, and from May 5 to July 3, 1990 (Lapakko and Antonson 1989c, 1990c; Lapakko et al. 1998). Operation was terminated in 1988 and 1989 when freezing conditions were impending. The bed clogged persistently throughout the study and, consequently, the limestone was replaced with a coarser-sized limestone (6.4 to 38.1 mm) July 12, 1990 (Lapakko et al. 1998b).

The total flow volumes through the fine particle-size limestone bed during 1988, 1989, and 1990 were 580, 6600, and 3600 m<sup>3</sup>, respectively, yielding an average flow of 13, 25, and 45 bed volumes per day, respectively. The bed was 100% efficient in neutralizing acid in the seepage, raising the pH from approximately 5.1 to 7.0, and the net alkalinity from approximately -46 mg CaCO<sub>3</sub>/L to 28 mg CaCO<sub>3</sub>/L. Copper removal by the bed increased each year, reaching 68% in 1990. Zinc removal also increased from about 12% in 1988 and 1989 to 42% in 1990. Nickel and cobalt concentrations were reduced by approximately 10% throughout the study. Treatment efficiency for acid neutralization and trace metal removal were not influenced by the flow volume treated or the detention time for the ranges observed in this study.

The average rates of acid neutralization by the fine particle-size limestone bed were 14, 32, and 72 mg CaCO<sub>3</sub>/s in 1988, 1989, and 1990 respectively, implying that 0.84 T of limestone was dissolved during the operation of this bed. The release rate was independent of the volume of treatment, indicating that the treatment capacity of the bed was not taxed. The release rate did increase with flow, indicating that for the range of flows observed, the initial reaction of the Seep 1 drainage with the limestone was relatively rapid. Although the bed provided acceptable elevation of pH and net alkalinity, as well as some reduction in trace metal concentrations, the observed flow impedance was a problem which had to be addressed.

Larger-sized limestone particles were tested from July 12 to August 6, 1990, and although no overflow occurred, treatment efficiency decreased below acceptable levels. Total flow through this

bed during the 24 day period of operation was 790 m<sup>3</sup>, or 23 bv/day. However, the bed was only 25% efficient in neutralizing acidity in the seepage. The mean effluent pH only reached 4.9, and the effluent net alkalinity averaged -64 mg CaCO<sub>3</sub>/L. Furthermore, no more than 10% of copper, zinc, nickel, or cobalt was removed from the drainage. The mean rate of acid neutralization was a nominal 10 mg/s, indicating that only 0.02 T of limestone was dissolved.

The flow rates were too high to allow an adequate detention time for the larger limestone particles to effectively treat Seep 1 drainage quality. The rate of calcite dissolution is proportional to surface area. Since the surface area of the fine particles was approximately seven times that of the coarse particles, their dissolution rate would be approximately seven times faster than those of the coarse particles. It would therefore be expected that a limestone bed using the larger particles would require a detention time seven times that of the fine particles for adequate acid neutralization to occur. To achieve this detention time, a minimum bed volume of 3024 L would be required. However, only 25% of the Seep 1 drainage acidity was neutralized by the large particles in the limestone bed. This indicates that the bed volume should be increased by at least a factor of four to achieve adequate neutralization for the flow rates encountered. Additional investigation will be necessary to determine the actual bed volume required to neutralize Seep 1 drainage.

## **5.5. Subaqueous disposal.**

Five laboratory experiments and one field experiment were conducted to examine the effectiveness of subaqueous disposal and subaqueous disposal with various barrier layers for controlling the oxidation of sulfide minerals present in mine wastes. 1) Unmodified subaqueous disposal tests were initially conducted in 2-liter Erlenmeyer flasks. 2) Subsequent tests were conducted in 2-inch-diameter columns to describe the release of sulfate as a function of sulfidic mine waste depth for two different mine waste particle sizes. 3) In a second phase of the Erlenmeyer flask experiment, composted yard waste was added to some of these flasks to determine if organic amendments would further inhibit sulfide oxidation. 4) Composted yard waste and fresh rock, as well as controls for compost and rock, were subjected to subaqueous dissolution in the laboratory. 5) A column experiment was conducted to determine the effectiveness of taconite tailings, yard waste compost/tailings mixtures, and limestone layers above tailings as potential oxygen diffusion barriers above sulfidic mine waste. 6) Barriers of tailings, a yard waste compost/tailings mixture, and limestone are presently under examination in small scale field tests.

### **5.5.1. Unmodified subaqueous disposal.**

#### **5.5.1.1. Laboratory flask experiments.**

The first 120 weeks of the flask experiment were summarized by Lapakko (1994c). The experimental objective was to determine the effect of three different subaqueous disposal techniques on the oxidation of sulfide minerals present in Virginia Formation hornfels rock containing about

5.5 percent sulfur and about 14 wt% pyrrhotite ( $\text{Fe}_{0.9}\text{S}$ ). The subaqueous techniques were unmodified subaqueous disposal, subaqueous disposal with alkaline addition, and pretreatment (rinsing and neutralization) of rock prior to subaqueous disposal and subsequent alkaline addition. The pH of drainage from the two unsaturated controls, representing on-land disposal, ranged from 3.7 to 4.2 during the initial 100 weeks, then decreased rapidly to 3.2 at 120 weeks. During the first 100 weeks the sulfate release rates averaged roughly  $2.0 \times 10^{-12}$  mol/g rock·second; concurrent with the pH decrease, rates for controls increased to  $5.6 \times 10^{-12}$  and  $13 \times 10^{-12}$  mol per gram rock per second. For unmodified subaqueous disposal, pH declined steadily from 4.5 initially to 3.5 after 120 weeks. Pyrrhotite oxidation rates for the three subaqueous disposal techniques were  $1.5 \times 10^{-12}$ ,  $1.7 \times 10^{-12}$ , and  $2.2 \times 10^{-12}$  mol per gram rock per second, respectively. With the exception of some initial rapid sulfate release from rock that was not pretreated, these rates were relatively constant over the course of the experiment. The rates observed in the laboratory were used, along with oxygen transport theory, to determine acid production rates for disposal of similar mine waste in a flooded open pit.

#### 5.5.1.2. Laboratory column experiments.

Assuming oxygen transport was limited by diffusion through a quiescent layer of water, it was estimated that the depth of solids in the flasks (see previous section) was near that at which oxygen transport became limiting. Due to the uncertainty of values for variables necessary for this calculation, an experiment was conducted to 1) determine the depths of fine ( $0.053 < d \leq 0.149$  mm, 1.22 percent S) and coarse ( $0.635 < d \leq 1.905$  mm, 0.6 to 1.0 percent S) sulfidic Duluth Complex rock at which oxygen transport limited the rate of sulfide mineral oxidation and 2) better estimate values for oxygen transport variables for the materials used. Bed depths of 1 to 20 cm were used for the fine particles, and two standard Wet-Dry Cycle reactors were added after the columns were underway. Coarse particle bed depths of 5 to 150 cm were used. A 25-cm depth of water was maintained above the submerged beds, and unsaturated columns were run at three depths of fine and coarse particles for comparison with oxidation rates under saturated conditions.

The depth at which oxygen transport limited the rate of sulfide mineral oxidation in the fine and coarse tailings was on the order of 20 and 100 cm, respectively. The respective maximum sulfate release rates observed were  $2.5 \times 10^{-2}$  and  $1.5 \times 10^{-2}$   $\mu\text{mole}/\text{m}^2\text{s}$  ( $\text{m}^2$  represents the horizontal cross sectional area of the bed). These values are about an order of magnitude higher than those preliminarily predicted based on oxygen diffusion alone, perhaps due to advective oxygen transport due to thermal currents.

Although higher than the mathematically predicted rates, sulfate release from the subaqueous bed was lower than that from the unsaturated beds. Sulfate release from the deeper fine unsaturated columns was apparently limited by formation of a saturated layer at the top of the bed and, consequently, duplicate 75-g masses were subjected to unsaturated oxidation in standard MN DNR wet-dry cycle reactors to obtain data for an unsaturated condition. The weekly sulfate release from these reactors ( $3.0 \times 10^{-2}$   $\mu\text{mole}/\text{m}^2\text{s} = 0.50$   $\mu\text{mole}/\text{wk}\cdot\text{g rock}$ ) exceeded the observed range of  $1.2 \times 10^{-2}$  to  $2.5 \times 10^{-2}$   $\mu\text{mole}/\text{m}^2\text{s}$  from all masses of saturated tailings (38 to 555 g). The sulfate release

rates (per unit cross-sectional area) for the unsaturated coarse particle bed depths of 5, 50, and 150 cm were 1.5 to 3 times those for the corresponding saturated beds.

The sulfate release from the unsaturated fine and coarse rock was in good agreement with rates previously reported for unsaturated Duluth Complex rock. Release per unit mass unsaturated fine rock ( $0.50 \mu\text{mol}/\text{wk}\cdot\text{g}$  rock) was in good agreement with average values previously reported by Lapakko (1993a) for similarly sized samples with sulfur contents of 1.12 and 1.16 percent ( $0.59$  and  $0.31 \mu\text{mol}/\text{wk}\cdot\text{g}$  rock, respectively). Sulfate release from the unsaturated beds averaged  $0.017 \mu\text{mole}/\text{g}\cdot\text{week}$ , which agreed well with the  $0.02 \mu\text{mole}/\text{g}\cdot\text{wk}$  rate observed for the 0.25-0.75 inch fraction of 0.9-percent-sulfur gabbro (Lapakko et al. 1995).

The two experiments discussed above revealed that separating sulfidic mine waste from the atmosphere with a layer of water would reduce the rate of oxidation of sulfide minerals present. However, oxidation would continue and possibly produce acidic waters. Consequently, various modifications to subaqueous disposal are presently being examined.

## **5.5.2. Subaqueous disposal with modifications.**

### **5.5.2.1. Organic amendment flask and beaker experiments.**

The potential benefit of adding an oxygen consuming layer between sulfidic rock and the overlying water in the flasks experiment is under examination (MN DNR Hibbing laboratory, unpublished data). After approximately 4.5 years the addition of alkalinity to the flasks was terminated (see above), and 75 grams of yard waste compost was added to one of each pair of duplicate reactors. The quality of water was monitored for an additional year, at which time the pH of water in the three reactors receiving no compost was in the range of 3.4 to 4.3. For reactors receiving compost, the pH remained near seven or, in the case of the initial unmodified subaqueous treatment, increased to this level shortly after the addition. After 26 weeks of reaction, the pH in one of the compost amendment reactors (initial treatment 3) decreased below pH 6.0. At the end of the period of record, the pH in the two remaining organic amendment reactors was in the upper sixes to the lower sevens. Rates of sulfide oxidation were calculated for the different disposal techniques based on the rate of sulfate appearance in solution. The aqueous concentrations of phosphorous, ammonia-ammonium nitrogen, total Kjeldahl nitrogen, nitrate, and nitrite from the organic substrate were also determined. These results have not been formally analyzed and compiled.

The solids in the previous experiments had been weathering in a subaqueous environment for roughly 4.5 years prior to the addition of compost. A second experiment was begun using six 4-liter beakers: two composted yard waste controls (75 g/3.6 L), two unleached mineralized Virginia Formation hornfels controls (4.47% S, 200 g/3.6 L), and two with the compost (75 g/3.6 L) and hornfels rock (200 g/3.6 L). The composted yard waste controls were run for 20 weeks and pH was in the typical range of 7.5 to 7.8. The rock controls initially had pH values in the upper fours, then

gradually decreased to near 3 at week 91. The pH for the combined rock and compost was initially in the mid-sevens, dropped below 6.0 at week 113, and decreased to the mid-fives at week 125. In contrast, the solids subjected to the initial subaqueous oxidation (in the aforementioned flask tests) maintained pH above 6 for 179 weeks. It is possible that during the 224-238 weeks of subaqueous oxidation in the previous test, a) some of the more reactive sulfides were removed or b) the sulfide mineral surface had become less reactive. Such a reduction in reactivity could be the result of formation of a leached layer on the pyrrhotite. The difference in effectiveness may also have been due to differences in the initial compositions of the rock and/or compost in the two experiments. The results have not been formally analyzed and compiled.

#### **5.5.2.2. Column experiment on subaqueous disposal plus barrier layers.**

A second laboratory experiment, conducted in columns, is in progress to examine the effect of placing various barriers above sulfidic wastes (-4/+14 mesh rock) disposed in a subaqueous setting. The intent of these barriers is to further inhibit oxygen transport to the mine waste and, therefore, decrease the rate of sulfide mineral oxidation. The barriers under examination are tailings (1, 2, 3, 5, 10 cm depths), tailings/yard waste compost mixtures (0.1 percent compost with tailings at depths of 1, 3, 10 cm; 0.5 and 1.0 percent compost with tailings at 3 cm depth), and a layer of limestone above tailings (1 cm limestone over tailings depths of 0, 1, 3, 10 cm). Controls were included for unamended -4/+14 mesh rock and unscreened -3/4-inch rock in a subaqueous setting, and -4/+14 mesh rock in an unsaturated condition. At present little data on this experiment is available.

#### **5.5.3. Field scale tests on subaqueous disposal plus barrier layers.**

A field test examining the effectiveness of limestone, tailings, and a tailings compost mixture above sulfidic rock in a subaqueous environment is presently in progress at the MN DNR Research Site in Hibbing. The subaqueous tests are being conducted in large cylindrical tanks (d = 46 in., h = 120 in.), fitted with a 30 mil PVC liner. Inside the PVC liner was a filter fabric liner which extended to a height of 48 inches. Wells (i.d. = 1 in.) were installed to sample at distances of 3 and 39 inches from the bottom of the tanks:

The tanks were filled to a depth of 48 inches with -3/4-inch Duluth Complex rock, originally collected from the second Arimetco bulk sample site and subsequently crushed at the NRRI Coleraine Research Center. The sulfur contents of composites from each of the four tanks averaged 0.66% (0.63 to 0.69%). These values compare favorably with values determined for the same rock in the column experiments (0.63%), a composite sample taken from the barrels in which the samples were shipped (0.71%), and two grab samples taken by the NRRI from a larger pile of this material at Coleraine (0.76%).

The rock was placed into the tanks 5 November 1996, and water from the Hibbing Taconite Scranton Mine pit was added to the tanks from above (to a level one foot from the top of the tank) on 10

December 1996. The bottom port and surface water were sampled eight times and the middle port six times prior to the addition of barrier layer amendments. In August 1997, water was drained from the tanks and well water was added from below to the surface of the rock. Water addition to the control tank was continued to a level one foot from the top of the tank.

To the remaining three tanks, the amendments were added prior to filling the tanks to this level. A 53 liter (14 gallons) volume of each amendment was added, representing an amendment depth of approximately 4.4 cm (1.75 inches). The mass additions of limestone, tailings, and tailings plus compost were 87 kg, 81 kg, and 81 kg, respectively (191, 179, 179 lbs). The limestone and tailings were added on 26 August and the tailings/compost mixture on 27 August. The tailings/compost mixture contained 0.406 kg dry compost, or five percent of the mixture. Over time, water quality samples will be collected from the two well depths and the surface water to determine the rate of sulfate release and, by implication, the rate of sulfide mineral oxidation in the various settings. The first samples were collected on 28 August 1997 (week 0).

Two unsaturated tanks (d = 48 in., h = 42 in.) were also established to generate comparative water quality data for an on-land disposal scenario. These tanks were fitted with 1-inch slotted PVC outlet pipe on the bottom and were filled to a height of 38 inches with the same Duluth Complex rock. Subsequently a bulk density of 106.5 lb/cu ft (also 37% porosity, 2.7 specific gravity) was determined, indicating the rock mass was approximately 1930 kg. On 28 August 1997, 65 gallons of tap water was added to each tank to check for plumbing leaks and to attain field capacity. A grab sample (week 0) was collected on the same day from the initial drainage. Subsequent input to the tank will be limited to precipitation.

Through week 222, pH of water in the four subaqueous treatments ranged from 7.0 to 8.9, and values did not vary markedly among the four tanks. Values for all subaqueous tanks tended to be higher in the surface water. In contrast, pH values for the unsaturated controls at week 222 ranged from 4.2 to 4.5.

## 6. REFERENCES

- Alpers, C.N., Blowes, D.W., Nordstrom, D.K., Janbor, J.L. 1994. Secondary minerals and acid-mine water chemistry. In Short Course Handbook on Environmental Geochemistry of Sulfide Mine Wastes, Waterloo, Ontario, May 1994. Mineralogical Association of Canada. p. 247-270.
- Antonson, D. A., Lapakko, K. A. 2000. Archean greenstone laboratory dissolution experiment. MN Dept Nat. Res., Div. of Lands and Minerals, St. Paul, MN 38 p.
- Berndt, M.E. 1998. Computer simulations of As, Mo, Mn, and F mobility during in-pit disposal of taconite tailings in the Minorca Pit, Virginia, Minnesota. In fulfillment of a contract to the Minnesota Department of Health, Environmental Health Division, Health Risk Assessment Unit. 22 p plus appendices.
- Berndt, M.E., Lapakko, K.A. 1997a. Mineral solubility and surface adsorption constraints on trace element mobility during in-pit disposal of taconite tailings. In SME Conf. Proc. April 23-24, Duluth, MN.
- \_\_\_\_\_. 1997b. Chemistry of water associated with taconite processing and tailings reactions in the Mesabi Iron Range district, NE Minnesota. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 69 p plus appendices.
- Berndt, M.E., Lapakko, K.A., Jakel, E. M. 1998a. In-pit disposal of taconite tailings. Progress report: July 1 - December 31, 1997. 9 p plus appendices.
- \_\_\_\_\_. 1998b. In-pit disposal of taconite tailings: geochemistry. Progress Report through June 30, 1998. 40 p plus appendices.
- \_\_\_\_\_. 1999. In-pit disposal of taconite tailings: geochemistry. Final report. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 77 p plus appendices.
- Brown, R. 1989. Water management at Brenda Mines. In Proc. of the Thirteenth Annual British Columbia Mine Reclamation Symposium. June 7-9, 1989, Vernon, British Columbia. p. 8-17.
- Caruccio, F.T., Geidel, G., Pelletier, M. 1980. Occurrence and prediction of acid drainages. In proceedings on Surface Mining Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY, pp. 437-443.
- Cravotta, C.A. III. 1994. Secondary iron-sulfate minerals as sources of sulfate and acidity: Geochemical evolution of acidic ground water at a reclaimed surface coal mine in Pennsylvania. In Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Series No. 550; American Chemical Society: Washington, DC, 1993. p. 343-364.

Dewar, S. 1996. Letter from Steven Dewar, MN DNR Division of Lands and Minerals to Mike Sterk, LTV Steel Mining Company, dated 29 October 1996.

Dobrokhotov, G. R., Maiorova, E. V. 1962. Kinetics of autoclave leaching of chalcopyrite. *Zhurnal Prikladnoi Khemii*, 35 (8): 702-1709.

Doctor, D., Leopold, E. M., Lapakko, K. A. 2001. Carbonate mineral dissolution: Reaction rates and mechanisms. Literature summary funded by the Minnesota Legislature Appropriations for Environmental Cooperative Research. MN. Dept. Nat. Resources, Div. Lands and Minerals. St. Paul, MN. 18 p. plus appendices.

Eary, E. L., Schramke, J. A. 1990. Rates of inorganic oxidation reactions involving dissolved oxygen. *In* *Chemical Modeling of Aqueous Systems II*, Melchior, D. C. and Basset, R. L. eds. ACS Symposium Series 416, American Chemical Society, Washington, D. C. 556 p.

Eger, P. 1992. Wetland treatment for trace metal removal from mine drainage: The importance of aerobic and anaerobic processes. *Wat. Sci. Tech.* Vol. 29, No. 4. p. 249-256.

Eger, A. P., Johnson, B., Hohenstein, G. 1979. 1978 DNR/AMAX Field leaching and reclamation program: Progress report on the leaching study. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 161 p.

Eger, P., Johnson, B., Otterson, P. 1977. Field studies: Leaching, metal transport and metal pathways. Progress report to the Minnesota Environmental Quality Board Regional Copper-Nickel Study. 164 p.

Eger, A. P., Lapakko, K. A. 1980a. Leaching and chemical transport at the Erie Mining Company Dunka Site: A data summary, 1976-1979. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 117 p. plus appendices.

\_\_\_\_\_. 1980b. Transport of chemical constituents present in mining runoff through a creek system. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 47 p. plus appendices.

\_\_\_\_\_. 1980c. Environmental leaching of Duluth Gabbro under laboratory and field conditions: Oxidative dissolution of metal sulfide and silicate minerals. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 340 p.

\_\_\_\_\_. 1981. The leaching and reclamation of low-grade mineralized stockpiles. *In* Proc. 1981 Symposium on Surface Mining Hydrology, Sedimentology and Reclamation. Lexington, KY. p. 157-166.

\_\_\_\_\_. 1985. Heavy metals study progress report on the field leaching and reclamation program:

1977-1983. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 53 p. plus appendices.

\_\_\_\_\_. 1988. Nickel and copper removal from mine drainage by a natural wetlands. In Proc. 1988 Mine Drainage and Surface Mine Reclamation Conference, April 19-21, 1988, Pittsburgh, PA. V. 1. Mine Water and Mine Waste. U.S.D.I. Bureau of Mines IC9183. p. 301-309.

\_\_\_\_\_. 1989. The use of wetlands to remove nickel and copper from mine drainage. In Constructed Wetlands for Wastewater Treatment. 1989. D.A. Hammer, ed. Presented at the International Conference on Constructed Wetlands for Wastewater Treatment, June 13-17, 1988, Chattanooga, Tennessee. p. 780-787.

Eger, A.P., Lapakko, K. A., Chamberlain, P. G. 1984. Mixed disposal of waste rock and tailings to reduce trace metal release from waste rock. In Proc. 1984 Symposium on Surface Mining Hydrology, Sedimentology and Reclamation. Lexington, KY. p. 49-56

Eger, A.P., Lapakko, K. A., Otterson, P. 1980a. Trace metal uptake by peat: Interaction of a white cedar bog and mining stockpile leachate. In Proc. of the 6th International Peat Congress. Duluth, MN. Aug. 17-23, 1980. p. 542-547.

Eger, A. P., Lapakko, K. A., Weir, A. 1980b. Heavy metals study: 1979 progress report on the field leaching and reclamation program, and the removal of metals from stockpile runoff by peat and tailings. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 95 p. plus appendices.

\_\_\_\_\_. 1981a. The environmental leaching of stockpiles containing copper-nickel sulfide minerals: A study of chemical release, chemical transport, and mitigation conducted at Erie Mining Company's Dunka Mine, Babbitt, Minnesota, 1976-1980. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 62 p. plus appendices.

\_\_\_\_\_. 1981b. Heavy metals study: 1980 progress report on the field leaching and reclamation program. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 31 p. plus appendices.

Eger, P., Wagner, J., Melchert, G.. 1996. Wetland treatment of mine drainage. In Successes and Failures: Applying Research Results to Insure Reclamation Success. Proc. 13<sup>th</sup> National Meeting ASSMR, Knoxville, TN, May 18-23, 1996. p. 580-89.

\_\_\_\_\_. 1997. The use of a peat/limestone system to treat acid rock drainage. In Proc. Fourth Internat. Conf. on Acid Rock Drainage. Vancouver, B.C., Canada. p. 1195-1209.

\_\_\_\_\_. 1998. Mine closure - can passive treatment be successful? In Proc. 25<sup>th</sup> Anniversary and 15<sup>th</sup> Annual National Meeting of the American Society for Surface Mining and Reclamation (ASSMR), St. Louis, MO, May 16-21. p. 263-271.

Eisenreich, S. J., Hoffmann, M. R., Carriker, N., Lapakko, K. A. Goldman, L. 1977a. Kinetics and mechanism(s) of metal sulfide release from mining derived solids. Progress report to Minnesota Environmental Quality Board Regional Copper-Nickel Study, July 1, 1977. 93 p..

Eisenreich, S.J., Hoffmann, M.R., Lapakko, K.A. 1977b. Progress report to Copper-Nickel Regional Task Force: Rates, mechanism and control of metal sulfide leaching from gabbro mining related solids, January 1977. Report to the Minnesota Environmental Quality Board Regional Copper-Nickel Study.

Garrels, R. M., Christ, C. L. 1965. Solutions, minerals, and equilibria. Freeman, Cooper and Company, San Francisco, CA.

Gottschalk, V.H. Buehler, H.A. 1912. Oxidation of sulfides (second paper). Econ. Geol. 7, p. 15-34.

Hem, J. D. 1970. Study and interpretation of the chemical characteristics of natural water. Geological Survey Water-Supply Paper 1473 Washington: 363 p.

Hewett, M. J. 1980. Hydrology of stockpiles of sulfide bearing gabbro in northeastern Minnesota. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 184 p.

Holdren, G. R., Berner, R. A. 1979. Mechanism of feldspar weathering - 1. Experimental Studies. Geochim. Cosmochim. Acta 43: 1161-1171.

Hornberger, R. J., Lapakko, K. A, Krueger, G. E., Bucknam, C. H., Ziemkiewicz, P. F., van Zyl, D. J. A., and Posey, H. H. 2000. The acid drainage technology initiative. In Proc. Fifth Int. Conf. Acid Rock Drainage, SME, Littleton, CO, p. 41-50.

Jakel, E.M., Lapakko, K. A. 1999a. Pyrite oxidative dissolution rates, products, and mechanisms: Annotated bibliography. MN Dept. Nat. Res. Div. Minerals. St. Paul, MN. 51 p.

\_\_\_\_\_. 1999b. Pyrrhotite oxidation, reaction rate, mechanism, and controlling variables. Status report. MN Dept. Nat. Res. Div. Minerals, St. Paul, MN. 12 p. plus appendices.

\_\_\_\_\_. 1999c. Taconite tailings in-pit disposal field tank experiments: data summary. MN Dept. Nat. Resources. Division of Lands and Minerals. 48 p. plus appendices.

\_\_\_\_\_. 1999d. In pit disposal of taconite tailings: Manganese oxidation experiments. Status report. MN Dept. Nat. Res. Div. Lands and Minerals. 23 p. plus appendices.

\_\_\_\_\_. 1999e. In-pit disposal of taconite tailings: The Snively Pit as US-Minntac, Mountain Iron, MN. MN Dept. Nat. Res. Div. Lands and Minerals. 31 p. plus appendices.

\_\_\_\_\_. 1999f. Dry cover systems for mine waste mitigation. Status Report. MN Dept. Nat. Resour., Div. of Minerals, St. Paul. 27p. plus appendix.

Jakel, E.M., Lapakko, K.A., Berndt, M.E. 1998a. Taconite tailings in-pit disposal field tank experiments. Data summary, June, 1998. MN Dept. Nat. Res. Div. Lands and Minerals. 37 p. plus appendices.

\_\_\_\_\_. 1998b. Potential sources and sinks of manganese, fluoride, boron, arsenic, and molybdenum in taconite plant process waters. MN Dept. Nat. Res. Div. Lands and Minerals. 16 p. plus appendices.

Kleinmann, R.L.P., Crerar, D.A., Pacelli, R.R. 1981. Biogeochemistry of acid mine drainage and a method to control acid formation. Mining Eng. March 1981. p. 300-305.

Kelsey, P. D., Klusman, R. W., Lapakko, K. A. 1996. Equilibrium modeling of trace metal transport from Duluth Complex rockpile. 13<sup>th</sup> Annual National Meeting of the Am. Soc. for Surface Mining and Reclamation, May 18-23. Knoxville, TN. p. 671-680.

Kingston, G. A., Carillo, F. V., Gray, J. J., Mallory, P. 1970. Availability of U.S. primary nickel resources. BuMines IC8469. 57 p.

LTV Steel Mining Company. 1996. LTV Steel Mining Company Dunka Mine Updated Final Closure Plan, Revision 4, March 15, 1996. NPDES / SDS Permit No. MN 0042579. 35 p. plus figures and drawings.

Lapakko, K. A. 1980. The kinetics and mechanisms of the oxidative dissolution of metal sulfide and silicate minerals present in the Duluth Gabbro. M. S. Thesis, Univ. MN, Minneapolis, MN. 199 p. plus appendices.

\_\_\_\_\_. 1988a. Prediction of acid mine drainage from Duluth Complex mining wastes in northeastern Minnesota. In Proc. 1988 Mine Drainage and Surface Mine Reclamation Conference, April 19-21, 1988, Pittsburgh, PA. V. 1. Mine Water and Mine Waste. U.S.D.I. Bureau of Mines IC9183. p. 180-190.

\_\_\_\_\_. 1988b. Preoperational projection of metallic mine waste drainage quality. Proc. International conference on Control of Problems from Metal Mines. June 20-24, 1988, Roros, Norway. Federation of Norwegian Industries and State Pollution Control Authority of Norway.

\_\_\_\_\_. 1990a. Solid phase characterization in conjunction with dissolution experiments for prediction of drainage quality. In Mining and Mineral Processing Wastes, Proceedings of the Western Regional Symposium on Mining and Mineral Processing Wastes. Sponsored by Society for Mining, Metallurgy, and Exploration (SME), and the San Francisco Section, SME. May 30 - June 1, 1990, University of CA at Berkeley. p. 81-86.

\_\_\_\_\_. 1990b. Regulatory mine waste characterization: A parallel to economic resource evaluation. In Mining and Mineral Processing Wastes, Proceedings of the Western Regional Symposium on Mining and Mineral Processing Wastes. Sponsored by Society for Mining, Metallurgy, and Exploration (SME), and the San Francisco Section, SME. May 30 - June 1, 1990, University of CA at Berkeley. p. 31-39.

\_\_\_\_\_. 1991a. Non-ferrous mine waste characterization project. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 68 p. plus appendices.

\_\_\_\_\_. 1991b. Mine waste drainage quality prediction: A literature review. First draft to Western Governors' Association. MN Dept. Nat. Resour., Div. of Minerals. 50 p.

\_\_\_\_\_. 1992a. Recent literature on static predictive tests. In Emerging Process Technologies for a Cleaner Environment, S. Chander (ed.), Soc. for Mining, Metallurgy, and Exploration, Inc., Littleton. CO. p. 109-119.

\_\_\_\_\_. 1992b. Characterization and static testing of ten gold mine tailings. In Achieving Land Use Potential through Reclamation. Proc. 9th National Meeting ASSMR, Duluth, MN, June 14-18, 1992. p. 370-384.

\_\_\_\_\_. 1993a. Laboratory dissolution of blast hole samples of Duluth Complex rock: Report to the US Bureau of Mines Salt Lake City Research Center. Coop Agreement No. C0219003. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 40p.

\_\_\_\_\_. 1993b. Field dissolution of test piles of Duluth Complex rock: Report to the US Bureau of Mines Salt Lake City Research Center. Coop. Agreement No. C0219003. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 41p.

\_\_\_\_\_. 1993c. Non-ferrous mine waste characterization project: Final report. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 98 p.

\_\_\_\_\_. 1993d. Evaluation of tests for predicting mine waste drainage pH. Report to the Western Governor's Association. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 76p.

\_\_\_\_\_. 1993e. Laboratory dissolution of drill core samples of Duluth Complex rock: Draft report to the US Bureau of Mines Salt Lake City Research Center. Coop Agreement No. C0219003. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 28p. plus appendices.

\_\_\_\_\_. 1994a. Comparison of Duluth Complex rock dissolution in the laboratory and field. In Internat. Land Reclamation and Mine Drainage Conf. and the 3<sup>rd</sup> Internat. Conf. on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29. p. 419-428.

\_\_\_\_\_. 1994b. Evaluation of neutralization potential determinations for metal mine waste and a proposed alternative. Internat. Land Reclamation and Mine Drainage Conf. and the 3<sup>rd</sup> Internat. Conf. on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29. p.129-137.

\_\_\_\_\_. 1994c. Subaqueous disposal of mine waste: Laboratory investigation. In Internat. Land Reclamation and Mine Drainage Conf. and the Third International Conf. on the Abatement of Acidic Drainage, Pittsburgh, PA, April 24-29,. P. 270 - 278.

\_\_\_\_\_. 1996. Laboratory drainage quality from siltite-argillite and Duluth Complex rocks: Progress report to the US Bureau of Land Management, Salt Lake City, UT. Contract J910P62009. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN, 12p. plus appendices.

\_\_\_\_\_. 1998a. Laboratory drainage quality from siltite-argillite rock: Progress report to the US Bureau of Land Management, Salt Lake City, UT. Contract J91072015. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN, 41 p. plus appendices.

\_\_\_\_\_. 1998b. Laboratory drainage quality from Duluth Complex rock and assessment of test methods for waste rock dissolution. Final report to the US Bureau of Land Management, Salt Lake City, UT. Contract J91072015. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN, 18 p. plus appendices.

\_\_\_\_\_. 1998c. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks: Progress report on contract J910C82009 to the US Bureau of Land Management, Salt Lake City Office. MN Dept of Nat. Resources Division of Minerals. St. Paul, Minnesota, 21 p. plus appendices.

\_\_\_\_\_. 1999a. Laboratory drainage quality from Duluth Complex rock and assessment of test methods for waster rock dissolution. Report on Contract BLM J910C82009 to the U. S. Bureau of Land Management Salt Lake City Office. 32. p. plus appendices.

\_\_\_\_\_. 1999b. Laboratory drainage from siltite-argillite rock. Final appendices for contract BLM J910C82009 to the US Bureau of Land Management Salt Lake City Office.

\_\_\_\_\_. 1999c. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks: Report on contract J910C82009 to the US Bureau of Land Management, Salt Lake City Office. MN Dept of Nat. Resources Division of Minerals. St. Paul, Minnesota, 32 p. plus appendices.

\_\_\_\_\_. 1999d. Uncertainty in neutralization potential determination. In Summary Notes 5<sup>th</sup> Annual BC MEM-MEND 2000 Metal Leaching and ARD Workshop, Vancouver, B. C., Dec. 1998. Section B7, 13 p.

\_\_\_\_\_. 2001a. ADTI-MMS Annual Report, [www.mackay.unr](http://www.mackay.unr), 21 p.

\_\_\_\_\_. 2001b. Metal mine rock and waste characterization tools: An overview. Report on ADTI-MMS website. 30p.

Lapakko, K. A., Antonson, D. A. 1989a. Alkaline addition reactor experiments: April 1989 status report. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 28p.

\_\_\_\_\_. 1989b. Limestone column treatment of stockpile drainage: April 1989 status report. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 16p.

\_\_\_\_\_. 1989c. Seep 1 limestone bed: 1988 Progress Report. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 17p.

\_\_\_\_\_. 1990a. Laboratory experiments on the mixture of alkaline solids with sulfide bearing rock. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 37p. plus appendices.

\_\_\_\_\_. 1990b. Laboratory treatment of three acidic stockpile drainages by limestone columns. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 22p. plus appendices.

\_\_\_\_\_. 1990c. Pilot scale limestone bed treatment of the Seep 1 waste rock drainage. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 24p. plus appendices.

\_\_\_\_\_. 1990d. Treatment of waste rock drainage with limestone beds. In Proceedings of the Geological Association of Canada - Mineralogical Association of Canada Annual Meeting, Acid Mine Drainage Conference. May 16 - 18, 1990. Vancouver, British Columbia, Canada.

\_\_\_\_\_. 1991. Mixing of limestone with acid producing rock. In Proceedings of the Second International Conference on the Abatement of Acidic Drainage, September 16-18, 1991. Montreal, Quebec. p. 343-358.

\_\_\_\_\_. 1993. Oxidation of sulfide minerals present in Duluth Complex rock: A laboratory study. In Environmental Geochemistry of Sulfide Oxidation, ACS Symposium Series No. 550; American Chemical Society: Washington, DC, 1993. p. 593-607.

\_\_\_\_\_. 2000a. Laboratory drainage quality from Duluth Complex rock and assessment of test methods for waste rock dissolution. Final report on contract J910P82018 to the U. S. Bureau of Land Management Salt Lake City Office. 54 p. plus appendices.

\_\_\_\_\_. 2000b. Laboratory drainage quality from mafic-intrusive, tuffaceous-sedimentary, and weathered waste rocks: Final report on contract J910P82018 to the US Bureau of Land Management, Salt Lake City Office. 64 p. plus appendices.

\_\_\_\_\_. 2001. Laboratory drainage pH and sulfate release rates from the Archean Greenstone rock. In Securing the Future, Int. Conference on Mining and the Environment. Skelleftea, Sweden, p. 384-393.

Lapakko, K., Antonson, D., Jakel, E. 1998. Mine waste characterization and drainage mitigation: Research summary 1998. MN Dep. Nat. Resour., Div. Minerals, St. Paul, MN. 50 p.

Lapakko, K. A., Antonson, D. A., Johnson, A. 2001. Archean Greenstone laboratory and field dissolution experiments. Controlling mine drainage problems- New approaches for waste rock stockpiles. Final Report to Minerals Coordinating Committee. MN. Dept. Nat. Resources, Div. of Lands and Minerals, St. Paul, MN. 79 p. plus appendices.

Lapakko, K.A., Antonson, D.A., Wagner, J. 1997. Mixing of limestone with finely-crushed acid-producing rock. In Fourth Internat. Conf. on Acid Rock Drainage. Vancouver, B.C., Canada. p. 1345-1360.

\_\_\_\_\_. 1998. Mixing of alkaline solids with finely-crushed acid-producing rock. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 49 p.

\_\_\_\_\_. In progress. Laboratory treatment of three acidic stockpile drainages by limestone columns. MN Dept. Nat. Resour., Div. of Minerals, St Paul, MN.

\_\_\_\_\_. 2000. Mixing of rotary kiln fines with fine-grained acid-producing rock. In Proc. 5<sup>th</sup> Int. Conference on Acid Rock Drainage, SME, Littleton, CO, p. 901-910.

Lapakko, K.A., Antonson, D.A., Wagner, J., Jakel, E. M. 1998. Pilot scale limestone bed treatment of the Seep 1 waste rock drainage: 1990 status report. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 23 p. plus appendices.

Lapakko, K.A., Berndt, M.E., Jakel, E. M. 1998. Predicted water quality in open pits into which taconite tailings are disposed. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 23 p.

Lapakko, K.A., Brice W. 1998. Can industry-government partnerships work? Experiences in mine waste management research. SME Annual Meeting, Orlando, FL, March 9-11, 1998. Preprint 98-93. SME, Inc., Littleton, CO. 6p.

Lapakko, K. A., Eger, A. P. 1980a. Environmental leaching of trace metals from waste rock and lean ore stockpiles. In Proc. of the 53rd Annual Meeting Minnesota Section AIME and 41st Annual Mining Symposium, Jan. 16-18, Duluth, MN, p16-1 to 16-14.

\_\_\_\_\_. 1980b. Mechanisms and rates of leaching from Duluth Gabbro waste rock. Presented at SME-AIME Fall Meeting and Exhibit, Oct. 22-24, Minneapolis, MN, Preprint 80-367, 14 p.

\_\_\_\_\_. 1981a. Trace metal removal from mining stockpile runoff using peat, wood chips, tailings, till, and zeolite. In Proc. 1981 Symposium on Surface Mining Hydrology, Sedimentology and Reclamation. Lexington, KY, p105-116.

\_\_\_\_\_. 1981b. Transport of trace metals and other chemical components in mining runoff through a shallow bay. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 38 p. plus appendices.

\_\_\_\_\_. 1983. Passive treatment of sulfide stockpile runoff. In Proc. 1983 National Conference on Environmental Engineering, A. Medine and M. Anderson eds. ASCE, New York, p643-651.

\_\_\_\_\_. 1988. Trace metal removal from stockpile drainage by peat. In Proc. 1988 Mine Drainage and Surface Mine Reclamation Conference, April 19-21, 1988, Pittsburgh, PA. V. 1. Mine Water and Mine Waste. U.S.D.I. Bureau of Mines IC9183, p291-300.

Lapakko, K. A., Eger, A. P., Strudell, J. D. 1986a. Low-cost removal of trace metals from copper-nickel mine drainage. (Final report, Bureau of Mines Contract J0205047). U.S.D.I. Bureau of Mines NTIS # PB 87-186136. 103 p.

\_\_\_\_\_. 1986b. Trace metal sequestration by peat, other organics, Tailings, and soils: A literature review. (Final Report BuMines Contract J0205047). U.S.D.I. Bureau of Mines NTIS # PB 87-186144, 45 p.

Lapakko, K. A., Engstrom, J., Antonson, D. A. 1999. Non-ferrous mine waste characterization project: Project extension status. MN DNR, Division of Minerals, St. Paul, MN. 105 p. plus appendices.

Lapakko, K.A., Haub, J.N., Antonson, D.A. 1998. Effects of dissolution time and particle size on kinetic test results. SME Annual Meeting, Orlando, FL, March 9-11, 1998. Preprint 98-114. SME, Inc., Littleton, CO. 9p.

Lapakko, K.A., Jagunich, A. 1991. Sulfate release from the USX tailings basin and quantification of sulfate sources. MN Dept. of Nat. Resour., Div. of Minerals, St. Paul, MN. 34 p. plus appendices.

Lapakko, K. A., Jakel, E. M. 1999. Summary of potential impacts of taconite tailings disposal in the Minorca Pit on water quality in the Missabe Mountain Pit. Report to Rebecca Wooden, September 2, 1999. MN Dept. of Natural Resources, Div. Lands and Minerals. St. Paul, MN. 29 p. plus appendices.

\_\_\_\_\_. 2000. Detailed analysis of potential impacts of taconite tailings disposal in the Minorca Pit on water quality in the Missabe, Mountain Pit: Final Report. MN Dept. of Nat. Resources, 83 p. plus appendices.

Lapakko, K. A., Lawrence, R. W. 1994. Modification of the net acid production (NAP) test. In Proc. of the 17<sup>th</sup> Annual British Columbia Mine Reclamation Symposium, May 4 to 7, Port Hardy, British Columbia, p. 145-159.

Lapakko, K. A., Oberhelman, M. 1993. Water quality at potential dimension stone quarry sites in northern Minnesota. MN Dept. Nat. Resour, Hibbing, MN. 11p. plus appendices.

Lapakko, K. A., Strudell, J. A., Eger, A.P. 1983. Sulfide stockpile leachate flow through a tailing bed: Trace metal removal and flow modeling for a low maintenance treatment system. Proc. 1983 Symposium on Surface Mining Hydrology, Sedimentology and Reclamation. Lexington, KY, p.321-327.

Lapakko, K. A., Wagner, J. 1989. Trace metal concentrations in drainage from iron mining wastes. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 12 p. plus appendices.

Lapakko, K. A., Wessels, J. N. 1993. Dissolution of tailings from hydrothermal gold deposits. Poster presented at 1993 Current Activities Forum, Chisolm, MN, Oct. 14.

\_\_\_\_\_. 1994. Release of acid and trace metals from quartz-carbonate hosted gold mine tailings. In Proc. Institute on Lake Superior Geology, 40<sup>th</sup> Annual Meeting, Houghton, MI. Eds. Bornhorst, T.J. and McDowell, S.D. May 11-14, p.29.

\_\_\_\_\_. 1995. Release of acid from hydrothermal quartz-carbonate hosted gold-mine tailings. In Sudbury '95, Conf. on Mining and the Environment, May 28-June 1, Sudbury, Ontario, p. 139-148.

Lapakko, K. A., Wessels, J. N., Antonson, D. A. 1994. Characterization of environmentally weathered Duluth complex rock stockpiles. Current Activities Forum, October 27. abstract.

\_\_\_\_\_. 1995. Long term dissolution testing of mine waste. Report to the US EPA. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN, 85p.

Lapakko, K. A., White, W. W. III. 2000. Modification of the ASTM 5744-96 kinetic test. In Proc. 5<sup>th</sup> Int. Conference on Acid Rock Drainage. SME. Littleton, CO, p. 631-639.

Lawrence, R. W. 1990. Prediction of the behavior of mining and processing wastes in the environment. In Proc. Western Regional Symposium on Mining and Mineral Processing Wastes, F. Doyle (ed.), Soc. for Mining, Metallurgy, and Exploration, Inc., Littleton, CO. p. 115-121.

Leopold, E. M., Lapakko, K. A. 2000. Environmental mine waste management: Summary of prevention, control, and treatment strategies for problematic drainages. Progress report to the minerals coordinating committee. 54 p. plus appendices.

\_\_\_\_\_. 2001a. Pyrite oxidative dissolution: reaction rates and mechanisms. Annotated bibliography funded by the Minnesota Legislature Appropriations for Environmental Cooperative Research with US Bureau of Land Management, Utah State Office of Predictive Accelerated Weathering Test Project. MN Dept. Nat. Res. Div. Lands and Minerals, St. Paul, MN, 63 p. plus appendices.

\_\_\_\_\_. 2001b. Pyrrhotite oxidative dissolution: Reaction rates and mechanisms. Annotated bibliography funded by the Minnesota Legislature Appropriations for Environmental Cooperative Research with US Bureau of Land Management, Utah State Office of Predictive Accelerated Weathering Test Project. MN Dept. Nat. Res. Div. Lands and Minerals, St. Paul, MN, 12 p. plus appendices.

\_\_\_\_\_. 2001c. In-pit disposal of taconite tailings laboratory column simulations: Final sampling summary. 13p. plus appendix.

\_\_\_\_\_. 2001d. Environmental mine waste management: Strategies for the prevention, control, and treatment of problematic drainages. Final report to the minerals coordinating committee. 54 p. plus appendices.

LTV Steel Mining Company. 1996. LTV Steel Mining Company Dunka Mine: Updated Final closure Plan, Revision 4. March 15, 1996. NPDES/SDS Permit No. MN 0042579. 58 p. plus drawings.

Majima, H. , Peters, E. 1966. Oxidation rates of sulfide minerals by aqueous oxygen at elevated temperatures. Trans. of Metall. Soc of A.I.M.E. 236, p. 1409-1413.

McKay, D. R., Halpern, J. 1958. A kinetic study of the oxidation of pyrite in aqueous suspension. Trans. of Metall. Soc. of A.I.M.E., June.

MN DNR. 1987. Dunka data summary. Unpublished report. MN. Dept. Nat. Resour., Div. of Minerals. Hibbing, MN.

MN DNR. 1994. Dunka data summary: 1976-1991. Unpublished report. MN. Dept. Nat. Resour., Div. of Minerals. Hibbing, MN.

MN DNR. 1996. Dunka data summary: 1976-1993. Unpublished report. MN. Dept. Nat. Resour., Div. of Minerals. Hibbing, MN.

MN DNR. 1999. Environmental metal mine waste management: Ten year research plan. MN Department Nat. Resour. Div. of Lands and Minerals, Hibbing, MN, .

MN DNR. 2000. Cooperative mine waste research opportunity. MN Dept. Nat. Resources, Div. Lands and Minerals, Hibbing, MN, 10p.

Minnesota Department of Revenue. 1997. Personal communication with Tom Schmucker, Administrative engineer, Eveleth, MN.

Minnesota Environmental Quality Board. 1979. Regional copper-nickel study, Executive summary, volume 1. MN State Planning Agency, St. Paul, MN. 118 p.

Morey, G. B, et. al. 1982. MGS Map S-13, 1982.

Nelson, M. 1978. Kinetics and mechanisms of the oxidation of ferrous sulfide. Ph. D. Thesis, Stanford University, Palo Alto, CA.

Nordstrom, D.K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In Acid Sulfate Weathering. J.A Kittrick, D.S. Fanning, and L.R. Hossner (eds.), Soil Sci. Soc. America Spec. Pub. 10. Madison, WI. p. 37-56.

Otterson, P. H. 1978. Peat bogs and metal interactions: A literature review. Minnesota Environmental Quality Board Regional Copper-Nickel Study, June 1978. 16 p. plus appendix.

Phillips, E. Doctor, D., Leopold, E.M., Lapakko, K. A. 2001. Dissolution of silicate minerals present in Duluth Complex and Archean Greenstone formations. Literature summary funded by the Minnesota Legislature Appropriations for Environmental Cooperative Research. MN. Dept. Nat. Resources, Div. Lands and Minerals. St. Paul, MN. 35 p. plus appendices.

Pignolet-Brandom, S., Lapakko, K.A. 1990. Characterization of mine waste by QEM\*SEM automated scanning microscopy. Presented at the 1990 Annual Meeting and Exhibit 119th AIME Annual Meeting and WAAIME 74th Annual Meeting. February 26- March 1, 1990, Salt Lake City, UT. 6p.

Rice, N. 2001. Metallic mineral exploration lease information. Telephone conversation with Nancy Rice, Research Analyst Intermediate, MN. Dept. Nat. Resources, Div. Lands and Minerals. St. Paul, MN.

Sato, M. 1960a. Oxidation of sulfide ore bodies, I., Geochemical environments in terms of Eh & pH: Econ. Geology 55: 928-961.

\_\_\_\_\_. 1960b. Oxidation of sulfide ore bodies, 11. Oxidation mechanisms of sulfide minerals at 25°C. Econ. Geol. 55: 1202-1231.

Sato, M., Mooney, H. M. 1960. The electrochemical mechanism of sulfide self-potentials. Geophysics 25 (1): 226-249.

Singer, P.C., Stumm, W. 1970. Acid mine drainage: The rate determining step. Science, 167. p. 1121-1123.

Sobek, A.A., Schuller, W. A., Freeman, J. R., Smith, R. M. 1978. Field and laboratory methods applicable to overburden and minesoils. EPA 600/2-78-054. 203 pp.

Stevenson, R.J., Kreisman, P.J., Sather, N.P. 1979. Minnesota Regional Copper-Nickel Study. Vol. 3, Ch. 1, Geology and Mineralogy. MN Environ. Quality Board, 70 p.

Strudell, J. A. 1986. Observations on Billiken Creek drainage and Seep 1 area, 1982. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN. 9 p. plus appendices.

Strudell, J. A., Lapakko, K. A., Eger, A. P. 1984. Bob Bay study, 1983. MN Dept. Nat. Resour., Div. of Minerals, St. Paul, MN. 36 p. plus appendices.

STS Consultants Ltd. 1993. Final Closure Plan for Dunka Mine. Report to LTV Steel Mining Company. Hoyt Lakes, MN. 218 p. plus appendices.

\_\_\_\_\_. 1994a. Stockpile 8018 Capping, Dunka Mine NPDES Permit No. MN0042579. Report to LTV Steel Mining Company. Hoyt Lakes, MN. 6 p. plus appendix.

\_\_\_\_\_. 1994b. 051 Treatment System, Dunka Mine NPDES Permit No. MN0042579. Report to LTV Steel Mining Company. Hoyt Lakes, MN. 14 p. plus appendices.

Stumm, W., Morgan, J. J. 1981. Aquatic chemistry-An introduction emphasizing chemical equilibria in natural waters. John Wiley and Sons, Inc. New York. 780p.

Sung, W., Morgan, J. J. 1980. Kinetics and product of ferrous iron oxygenation in aqueous systems. Environ. Sci. Technol. 14: 561-568.

Thingvold, D., Eger, A. P., Hewett, M. J., Honetschlager, B., Lapakko, K., Mustalish, R. 1979. Water resources. In Minnesota Environmental Quality Board Regional Copper-Nickel Study 3 (4): 217 p.

Wessels, J., Perala, J., Lapakko, K. 1991. Directory of mine waste characterization and drainage quality contacts in Western Governors' Association Member States. MN Dept. Nat. Resour., Div. of Minerals. St. Paul, MN.

White, W. W., III, Lapakko, K. 2000. Preliminary indication of repeatability and reproducibility of the ASTM-5744-96 kinetic test for drainage pH and sulfate release rate. In Proc. 5<sup>th</sup> Int. Conference on Acid Rock Drainage. SME. Littleton, CO. p. 621-630.

White W.W., III, Lapakko, K.A., Cox, R.L.. 1997. Effects of protocol variables and sample mineralogy on static-test NP. In Proc. Eleventh Annual Conference of the Society of Mineral Analysts, April 7-10, Elko, NV. p. 188-223.

\_\_\_\_\_. 1999. Static-test methods most commonly used to predict acid-mine-drainage-Practical guidelines for use and interpretation. In: The Environmental Geochemistry of Mineral Deposits, Part A: Theory and Background, G.S. Plumlee and M. Logsdon, eds., Society of Economic Geologists Reviews in Economic Geology, V: 7a, p. 325-338.